GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: 1/12/80

Project Title: Fixation and Remobilization of Radioactive Waste Materials in Near-Surface Repositories

Project No: E-26-660

Project Director: Dr. G.G. Eichholz

Sponsor: The Institute for Research, Development, and Engineering in Nuclear Energy (IRDEN); AMAF Industries, Inc; 103 Sterrett Building; P.O. Box 1100; Columbia, MD 21044

Agreement Period: From 10/31/80 Until 5/31/81 (R+D Perf and Rpt Period)

Type Agreement: Contract No. AMAF-R10-004 (under Prime Contract No. DE-AC01-80ET-41108/SB3-4-0-8(a)-80-C-733) and Amendment No. 1

Amount: $92,236 (not-to-exceed)

Reports Required: Program Implementation Plan; Monthly Letter Progress Reports; Final Technical Report

Sponsor Contact Person (s):

Technical Matters

Contractual Matters
(thru OCA)

Mr. Alfred G. Meyer
AMAF Industries, Inc.
103 Sterrett Building
P.O. Box 1100
Columbia, MD 21044
(301) 995-1919

Defense Priority Rating: None

Assigned to: Nuclear Engineering (School/Laboratory)

COPIES TO:

- Project Director
- Division Chief (EES)
- School/Laboratory Director
- Dean/Director—EES
- Accounting Office
- Procurement Office
- Security Coordinator (OCA)
- Reports Coordinator (OCA)
- Library, Technical Reports Section
- EES Information Office
- EES Reports & Procedures
- Project File (OCA)
- Project Code (GTRI)
- Other OCA Research Property Coordinator
  Project Code (OCA)

GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 11/19/81

Project Title: Fixation and Remobilization of Radioactive Waste Materials in Near-Surface Repositories

Project No: E-26-660

Project Director: Dr. G. G. Eichholz

Sponsor: The Institute for Research, Development and Engineering in Nuclear Energy (IRDEN)

n-b 25 33 6 5 Sr 133

Effective Termination Date: 9/30/81

Clearance of Accounting Charges: 11/20/81

Grant/Contract Closeout Actions Remaining:

- [x] Final Invoice and Closing Documents
- [ ] Final Fiscal Report
- [x] Final Report of Inventions
- [x] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

Assigned to: Nuclear Engineering (School/~~Laboratory~~)

COPIES TO:

Administrative Coordinator	Research Security Services	EES Public Relations (2)
Research Property Management	~~Reports Coordinator (OCA)~~	Computer Input
Accounting	Legal Services (OCA)	Project File
Procurement/EES Supply Services	Library	Other _____

FORM OCA 10:781

SCHOOL OF NUCLEAR ENGINEERING

E-26-660

Atlanta, Georgia 30332 (404) 894-3720

December 4, 1980

Dr. Robert M. Dixon
Director, IRDEN
Suite 500
44 Broad Street, NW
Atlanta, Georgia 30303

First Monthly Progress Letter - Our Project E26-660

Contract No. AMAF-R10-004

Dear Dr. Dixon:

The first month of the project necessarily was transitional in nature, particularly since the formal letter of authorization to start work was not received until November 25, 1980. Consequently, the work done largely reflects activities carried forward from previous work in anticipation of this project. At this time, staff consists of Dr. T. F. Craft, part time; Dr. H. E. Holoway; Miss M. B. Downes and Mr. M. R. Olin, graduate research assistants, assisted by other GRA's on state funds; with myself as project director.

A systematic search of the literature has been started, with emphasis on recent report literature, much of which has not yet appeared in any of the abstract journals. The science and technology of the disposal of radioactive wastes is a subject of widespread interest, being studied by many investigators. For this reason, the literature will be monitored continually and specific topics will be searched out in detail as need arises.

A general review of the subject area was presented at IRDEN as a seminar on December 2, 1980.

Experimental work has been concerned with three areas: adsorption of waste radionuclides on rocks, soils and suspended particulates, surface area determinations and studies on the activability in the GTRR reactor of various mineral suspensions.

Of particular interest to this project are the effects of the presence of organic complexants and other pollutants in infiltrating waters on the sorption and remobilization of dispersed waste ions. To study this, some experiments have been started using phosphates in solution and observing the adsorption of tracers on suspended kaolin particles in the presence of basalt as the host rock.

A number of static sorption tests have been carried out. The isotopes involved were neptunium-235 and technetium-95, and their distribution between kaolin particles and certain minerals have been measured. Determination of the effect of some additives on the partitioning of activity has begun. It was found, for instance, that the addition of $(NH_4)_2HPO_4$ to the Np-235/basalt/kaolin mixture increases the kaolin K_d value by nearly two orders of magnitude and the basalt K_d by a factor of four or more. To determine if these effects were due to the NH_4^+ ion or the phosphate ion, another experiment was performed in which $(NH_4)_2SO_4$ was

added. This produced a slight decrease in the kaolin K_d but a somewhat larger increase in the basalt K_d. Other additives will be used in future tests to explore the role of various ions.

An extensive series of tests have been conducted on the sorption of technetium-95 on basalt and sand. It was found that the addition of neither ammonium phosphate nor ammonium sulfate to the solution resulted in any significant changes in the tracer adsorption on kaolin or basalt. This is an area which is being investigated further.

Yours sincerely,

Geoffrey G. Eichholz
Regents' Professor

GGE/lm
cc: N. McHan (OCA)
T. F. Craft
A. Esogbue (ISyE)
L. E. Weaver

SCHOOL OF NUCLEAR ENGINEERING

Atlanta, Georgia 30332 (404) 894-3720

January 7, 1981

E 26-660

Dr. Robert M. Dixon
Director IRDEN
Suite 500
44 Broad St. NW
Atlanta, GA 30303

Second Monthly Progress Letter - Contract No. AMAF R10-004
Our Project E 26-660

Dear Dr. Dixon:

Apart from the break for the Christmas vacations, work has progressed during December in several directions. The literature search has been continued to update the information available on low-level waste repositories and retardation phenomena. Initial steps have been taken to arrive at a reasonable description of potential source terms and of the soil characteristics under saturated or vadose conditions.

Conceptual design has started on a small-scale test bed that will permit variable conditions of moisture content and moisture gradient and online tracing of radionuclide migration. It is expected that construction of such a test bed will be completed during January.

Experimental work has continued on the uptake of radiotracers on mineral samples in the presence of varying concentrations of phosphate or sulfate, on surface measurements by the ethylene glycol techniques and on column tests observing the retention of kaolin particulates as a function of particle concentration.

A revised work schedule has been drawn up and a draft renewal proposal has been submitted for inclusion in IRDEN's proposal to the U.S. Department of Energy.

Yours sincerely,

Geoffrey G. Eichholz
Regents' Professor

GGE/meb
cc: N. McHan (OCA)
T.F. Craft
A. Esogbue (ISyE)
L.E. Weaver

Filed 30 MAR '81

SCHOOL OF NUCLEAR ENGINEERING

Atlanta, Georgia 30332 (404) 894-3720

File E-26-660

February 4, 1981

Dr. Robert M. Dixon, Director
IRDEN - Suite 500
44 Broad St., N.W.
Atlanta, Ga. 30303

Third Monthly Progress Letter - Contract No. AMAF R10-004

Our project E 26-660

Dear Dr. Dixon:

Work has advanced fairly smoothly during the past month and satisfactory progress has been maintained.

Under Task 1 of the project outline, literature review was maintained. To develop a source term scenario a study has been made to characterize the nature of anticipated low level wastes as a means of predicting the quantities of such materials that may migrate into the environment at a future date. Data have been assembled on the type, composition and concentrations of waste material that may arise from fuel cycle activities and institutional wastes. Preliminary assessment of the locations and environmental parameters of existing low level waste sites has been obtained and coupled with NBS data on canister corrosion to facilitate prediction of time frames for the release of solidified wastes from metal drums.

Since some of the radioactive materials are solidified in concrete and polymer matrices, experimental data have been collected from the literature on leach rates of radionuclides of interest from such solids. With this information it is expected that some realistic predictions on radionuclide release can be made in the near future for the type of burial sites envisaged. No attention has been paid so far to considerations of water quality.

Under Task 2 column tests have been continued with activated kaolin particles to study their movement through mineral beds and their retardation as a function of particle concentration and bed material.

As a major activity a test box has been constructed to permit vertical flow tests in sand and soils under conditions of variable moisture and saturation to simulate wet or vadose soil conditions. This system is nearing completion and should undergo tests shortly.

Also under Task 3 work has continued on the effect of phosphates on the adsorption of neptunium on different minerals as a function of pH and water composition. This work will be extended shortly to the adsorption of Cs-137 and the effect of other complexants, such as EDTA and tannic acid.

Yours sincerely,

Geoffrey G. Eichholz
Regents' Professor

GGE/meb

cc: N. McHan (OCA)
T.F. Craft
A. Esogbue (ISyE)
L.E. Weaver

SCHOOL OF NUCLEAR ENGINEERING

Atlanta, Georgia 30332 (404) 894-3720

E-26-660

March 6, 1981

Dr. Robert M. Dixon
Director, IRDEN
Suite 500
44 Broad St., N.W.
Atlanta, GA 30303

Fourth Monthly Progress Letter - Contract No. AMAF R10-004
Our Project E26-660

Dear Dr. Dixon:

Except in one area, work has progressed well at the expected pace.

Under Task 1, substantial progress has been made to define a reasonable source term. This work is being written up and will be issued as a separate topical report, by Dr. Homer Holloway, which will be incorporated into the final report. The source term has been stated in terms of a Reference Containment Facility (RCF) to bring it in line with other similar studies.

Under Task 2, column tests have been continued on the migration of activated kaolin particles through mineral beds, principally sand, basalt and limestone. Subsidiary tests are under way to identify more clearly the nature of the activated sodium.

The major setback has been in the construction of the test box to permit flow tests in permeable media under varying moisture conditions. The box has been built but proved to be leaking despite various attempts to seal it. It has now been completely rebuilt, with a better grade of plywood, and is undergoing tests for water-tightness.

Attempts have been made to obtain "representative" soil samples from the Savannah River Lab. and we hope to get some after coping with various bureaucratic barriers.

Under Task 3, beaker tests have continued on the effect of phosphates on the absorption of Np-235 and Tc-95m on kaolin, basalt and sand at high pH values. As expected absorption is greatly reduced in the presence of phosphates in solution, almost independent of their concentration.

As part of the project, I expect to go to the Gatlinburg Symposium on the uncertainties associated with the Regulation of Geological Disposal of Radioactive Waste, March 9-13, where I will be one of the keynote speakers.

Yours sincerely,

Geoffrey G. Eichholz
Project Director

cc. N. McHan (OCA)
T. F. Craft
A. Esogbue (ISyE)
L. E. Weaver

GGE:wlw

SCHOOL OF NUCLEAR ENGINEERING

E-26-660

Atlanta, Georgia 30332 (404) 894-3720

April 7, 1981

Dr. Robert M. Dixon
Director, IRDEN
Suite 500
44 Broad St., N.W.
Atlanta, GA 30303

Fifth Monthly Progress Letter - Contract No. AMAF R10-004

Our Project E26-660

Dear Dr. Dixon:

Work has progressed steadily during the month, except for the week between academic quarters.

Under Task 1 work on defining the source term has been completed for the present. A topical report on the subject by Dr. H. Holloway has been completed and a copy is attached to this letter.

Under Task 2 the test box had to be completely rebuilt and now performs satisfactorily. Tests are underway with a sand bed to establish operating procedures and measurement protocols. The sand bed is too permeable to retain substantial amounts of moisture and actual test work will be done with more realistic soil samples. Assurances have been received from Savannah River Lab. that soil samples will be provided, but none have been received so far. Tests have continued to identify the nature and location of the activable sodium in our kaolin suspensions.

Under Task 3 absorption and desorption tests of Np-235 and Cs-137 on various minerals have been resumed in the presence and with later addition of phosphates and chelates. This work is expected to receive increased attention during the coming month.

As part of the project work, I attended the Gatlinburg Symposium on the Uncertainties Associated with the Regulation of Geologic Disposal of Radioactive Waste, where I presented one of the keynote addresses. I also participated in the Program Review of the Low-level Waste Disposal Program for EG&G.

Yours sincerely,

Geoffrey G. Eichholz
Project Director

cc. D. Hutchinson (OCA)
T. F. Craft
A. Esogbue
L. E. Weaver

GGE:wlw

Attachment

GEORGIA INSTITUTE OF TECHNOLOGY

SCHOOL OF NUCLEAR ENGINEERING

E26-660

Atlanta, Georgia 30332 (404) 894-3720

May 8, 1981

Dr. Robert M. Dixon
Director, IRDEN
Suite 500
44 Broad Street, NW
Atlanta, Georgia 30303

Sixth Monthly Progress Letter - Contract No. AMAF R10-004
Our Project E-26-660

Dear Dr. Dixon:

During the past months further work has been done to qualify operations with the test box using a sand. The pattern of movement through the bed has been studied in a preliminary fashion using a soluble dye as a visible tracer. A pulse injection system has been constructed consisting of an adjustable peristaltic pump and a spiral-shaped sprinkler system. This permits injection of the tracer solution in slow bursts to simulate slow seepage through the bed.

Tests have been performed to develop a consistent moisture testing procedure. The present procedure was found to be too primitive, and an improved approach is being sought at the moment. Following assurances from Savannah River Labs, a well-qualified soil sample is expected momentarily.

Under Task 3 substantial progress has been made in bench tests on the effects of phosphates and EDTA on tracer adsorption on minerals. As expected, phosphate addition inhibits adsorption of Cs-137 on most minerals and if added later, promotes desorption. A range of K_a values have been obtained, and the variation of pH with attainment of equilibrium has been followed. These tests continue, and a fair volume of data on both phosphate and EDTA additions is expected during the current month.

Work has continued to validate some of the delayed migration observations obtained in column tests with activated kaolin particles. Washing, centrifuging and pretreatment with potassium have indicated the existence of both structural sodium and sorbed sodium in some sample suspension. These tests continue.

In related activities I participated as one of the speakers in the IRDEN Workshop on Research Problems in Nuclear Waste Management at Tuskegee Institute on April 16, 1981. A renewal proposal has been submitted for continuation of this project beyond May 31, and it is hoped that a smooth transition will be contracted in good time.

Yours sincerely,

Geoffrey G. Eichholz
Regents' Professor

GGE/lm
cc: D. Hutchinson (OCA)
A. Esogbue (ISyE)
L. E. Weaver
T. F. Craft

SCHOOL OF NUCLEAR ENGINEERING

E-26-660

Atlanta, Georgia 30332 (404) 894-3720

June 15, 1981

Dr. Robert M. Dixon
Director, IRDEN
Suite 500
44 Broad Street, N.W.
Atlanta, GA 30303

Seventh Monthly Progress Letter - Contract No. AMAF R10-004
Our Project E26-660

Dear Dr. Dixon:

I am sending you herewith the usual monthly progress report in accordance with your instructions of March 11, 1981, to plan the work over a 12-month period. Please let me know immediately if you require a more formal report to cover the work done up to May 31, 1981.

Work during May continued along the lines started in the preceding month. Several tracer tests have been done to check the performance of the test box with sprinkler injection. A major effort has been made to develop a procedure to determine a moisture profile in the test bed. A large spike-type soil sampler has been obtained. Difficulties have been encountered in retaining wet sand columns in the sampler. A procedure of chilling the sampler pipe with liquid air has been tried and looks promising; it will be tested further. A substantial soil sample from a potential repository area at the Savannah River Plant site has been received and will be used initially in beaker adsorption tests.

Under Task 3 further results have been obtained on adsorption and desorption of Cs-137 on various mineral samples with initial addition of phosphates or addition of phosphates or EDTA after equilibration of the water-mineral systems. Significant changes with time were observed for tracer partition, pH and K_a values. However, there seemed to be no direct correlation between K_a and pH when comparing values before and after phosphate addition. This work continues. Some of the results obtained so far were reported at the Annual Meeting of the American Nuclear Society at Bal Harbor, Florida, this month.

Further work was done to identify the tracer components associated with previous column tests on particulate migration. By potassium treatment of the kaolin particles and gamma spectroscopy of the activated particles it was found that there was some desorbed Na-24 activity, but most of that activity was structurally fixed. In addition, manganese-56 was found and utilized to provide a column adsorption profile independent of the sodium distribution. Samples are being prepared for a longer irradiation to excite the long-lived Sc-46 activity in the kaolin which would enable us to prepare an adequate labeled stock suspension and to avoid doubt about sodium in solution.

We hope the contractual hiatus can be resolved rapidly and would welcome a stop-gap time extension of the old contract.

Yours sincerely,

Geoffrey G. Eichholz
Project Director

cc: G. D. Hutchison (OCA)
A. Esogbue (ISyE)
L. E. Weaver
T. F. Craft

GGE:wlw

FIXATION AND REMOBILIZATION OF RADIOACTIVE WASTE MATERIALS IN NEAR-SURFACE DEPOSITORY

Final Technical Report
Contract No. AMAF-R10-004
Project No. E-26-660

Geoffrey G. Eichholz
Project Director

Submitted to

The Institute for Research Development and Engineering
in Nuclear Energy; AMAF Industries, Inc.
Under Its Contract with the U. S. Department of Energy

School of Nuclear Engineeirng and Health Physics
Georgia Institute of Technology
Atlanta, Georgia 30332

November, 1981

NOTICE

Abstract

The problem of groundwater transport of leached low-level radioactive wastes in shallow repositories has been studied in four aspects: 1. a simple source term has been developed for such material to serve as a starting point in model calculations; 2. migration studies with soluble radioactive tracers in semipermeable media have been initiated to simulate transport under non-saturated conditions; 3. the effect of complexing agents on the sorption of dissolved ions on rock surfaces has been investigated and 4. the mobility of particulate vectors in soil media has been further studied to determine retardation parameters.

The work has shown that in a vadose region with some moisture retained in porous media at a certain horizon diffusional migration can be demonstrated, superimposed on a basically stationary front. The degree of absorption and desorption is strongly affected by the injection of complexants, such as phosphates or EDTA. Finally, the reality of a delayed component in particulate migration, that had been observed in previous work, was again encountered with a kaolin suspension, whose trace scandium content had been activated.

PROJECT STAFF

Geoffrey G. Eichholz, D.Sc., Project Director

T. Fisher Craft, Ph.D., Senior Research Scientist

Homer E. Holloway, Ph.D., Visiting Scientist

M. Beverley Downes, B.S., Graduate Research Assistant

Daniel P. Leddy, B.S., Graduate Research Assistant

Morse R. Olin, B.S., Graduate Research Assistant

Steven B. Willhoite, B.S., Graduate Research Assistant

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF FIGURES

LIST OF FIGURES (continued)

INTRODUCTION

Disposal of low-level radioactive wastes is typically planned to involve placement of sealed canisters or containers in trenches or blockhouses a few meters below surface. Any subsequent environmental effect of this waste is usually assumed to be due to infiltration of surface water, either by subsidence or surface seepage or by accidental human intrusion. It is then postulated that water will accummulate in the repository, attack or degrade the container followed by leaching or suspension of some of the radioactive material in that water, which may then slowly seep into the ground or overflow to surface.

Most repositories have been planned to be placed in a relatively impermeable, clayey soil, appreciably above the water table and usually on high ground to minimize standing water. The degree of infiltration of water can be minimized by proper design; however, to obtain a conservative estimate of any major consequences some incursion of water is assumed with slow, but non-negligible release of some of the more soluble waste ions over the operational life of the repository. Most calculational models then postulate migration of the waste ions through a saturated soil layer, controlled primarily by ion-exchange characteristics and sorption isotherms of a homogeneous soil barrier.

Such a model may not be very realistic, even in a relative rainy climate as encountered in the Eastern United States. Unless the design of the repository permits a substantial accumulation of water, a situation that can be readily controlled, it is more likely that water in the soil may move in cycles with spells of appreciable rain and water seepage

alternating with dry periods. Under such conditions the soil is not necessarily saturated and the conditions of waste movement are modified significantly.

Another feature of the vadose zone is the variable quality of the surface water that may enter the repository. Depending on the nature of the surface run-off and surrounding soil conditions and land use, such water may have an appreciable organic content and may contain various fertilizers, such as phosphates or nitrates, and other agricultural chemicals. These additions can be expected to modify significantly the soil-water interface parameters and the sorption isotherms. The work reported here was dedicated to a preliminary study of some of those conditions; it is hoped that it can be followed up by more definitive investigations.

The work has been organized into four tasks and will be reported under those headings. These tasks are:

1. Waste scenarios and source terms
2. Simulation of nuclide movement through soil
3. Remobilization and effects of complexants

and 4. Particulate migration

Waste Scenarios and Source Terms

In order to provide sufficient background information for planning, designing and siting low level waste management facilities (1-4) it is important to define the nature and scope of the waste involved. There have been numerous estimates of the quantities of waste involved and its probable form (e.g. 5-7), but many of them ignore the varying chemical nature

of the wastes, the possibility of bacterial action, and the possibility for non-steady conditions likely to exist inside the repository volume of interest over the projected period of concern.

To arrive at a reasonable estimate of the nature of waste material expected to be mobilized by invading water in a shallow burial site, an analysis of potential source materials has been conducted and the results issued as a self-contained topical report. This report, written by H.E. Holloway is attached as Appendix A. The quantities listed are based on "reasonable" corrosion rates of metal containers; it was also assumed that burial trenches would not remain continually immersed in water. Obviously, detailed numbers derived will depend on such assumptions and will be different for other sites.

Additional corrections would have to be made to allow for overflow, the "bathtub effect", or for a trench design with controlled drainage. These are matters for a projected follow-on project.

Another factor of major significance is the nature of the infiltrating water. Many of the calculational models assume a relatively "pure" water at neutral pH and derive both corrosion effects and sorption parameters on that basis. Actually, through contact with rocks and soil, dissolved ions and pH are substantially modified; Table 1 indicates some of the measured properties for water kept in contact with selected rock materials.

It is well-known that water, on standing, will show some algae growth and any water percolating through top soil will acquire some organic components (8,9). Such organic materials may well change the permeability of the soil and may result in the formation of anionic or non-sorbable complexes with some of the waste ions. In addition, both organic and

inorganic particulate matter is commonly found in water in the vadose zone (10,11). Such particles may well serve as carriers of adsorbed radioactive waste ions and extensive studies on that phenomenon have been conducted at Georgia Tech (12-14).

Table 1. Properties of Some Equilibrated Waters

Rock Material	Method of Production*	pH	Conductivity (μ mho/cm)
Basalt	Refluxed	7.59	55
Basalt	Stirred	8.08	180
Shale	Refluxed	6.96	630
Shale	Stirred	6.80	630
Limestone	Refluxed	8.74	450
Limestone	Stirred	8.27	320
Magenta dolomite	Refluxed	8.62	1600
Culebra dolomite	Stirred	8.54	265
Sand	Stirred	6.72	10

*Water and pulverized mineral in contact for 60 days or more.

Simulation of Nuclide Movement Through Soil

As mentioned above, movement of dissolved ions in the vadose zone is quite complex and dependent on many parameters. In the present project two particular aspects were investigated in detail. These were:

a. Movement of dissolved ions through soil under non-saturated conditions; and

b. Movement of fine suspended particulates through surface soils under slow-flow conditions.

These two sub-tasks will be discussed in turn.

A. Movement of ions in non-saturated soil.

Most impact assessments for waste repositories assume that saturated conditions persist in the underlying soil during any periods when any water flow can be postulated conservatively. This is also a matter of convenience since the theory of water flow through a permeable medium is well-developed for saturated conditions (16-17), whereas for unsaturated conditions it has to depend on such concepts as the "wilting point". For most soils, in the absence of a substantial reservoir of water on surface, water will drain through under gravity until the remaining moisture is retained on mineral surfaces by surface tension and capillary forces. Figure 1, from Ref. 18, illustrates the forces acting on the remaining water which result in a moist but not wet layer in the soil some distance below the surface.

The present studies were intended to determine the point at which migration is no longer tenable and to study migration conditions in soil

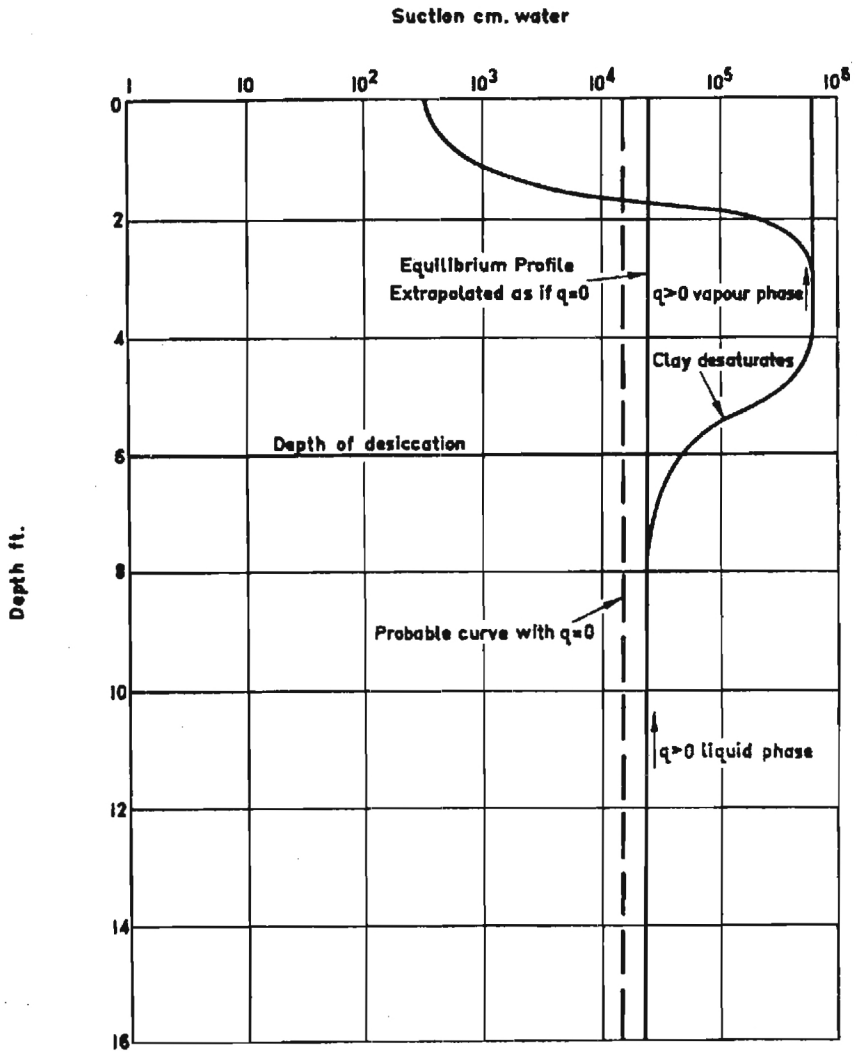


Figure 1. - Equilibrium Suction Profile Beneath the Surface Where Desiccation is Only a Few Feet in Depth.
q = vertical flux of moisture

that is cycled through saturated and drained conditions successively. Again, only preliminary results can be reported here.

Tests were conducted mainly on two media, a washed sand that had been used in previous research work, obtained from the Pennsylvania Glass Land Co. of Columbia, S.C., and a clayey soil sample from the Savannah River Laboratory site, Aiken, S.C. obtained through the kind services of Dr. John Pinder of the Savannah River Ecology Lab. This soil was described as follows (19):

"Dr. Corey sent a subsample of the soil to A & L Agricultural Laboratories (411 N. Third St., Memphis, TN, 38105: Phone: (901) 527-2780) for characterization. The sample (A & L Lab No. 4735) was a sandy clay loam with 65% sand, 2.8% silt, 31.2% clay, and 0.4% organic matter. Extractable P concentrations measured by the Weak Bray and $NaHCO_3$ methods were 5ppm and 7ppm, respectively. Exchangeable cation concentrations were 10ppm K, 20ppm Mg, and 100ppm Ca. The soil pH was 5.2; the cation exchange capacity was 1.1 meq/100g; the H^+ concentration was 0.4 meq/100g. Computed base saturations were 2.3% K, 15.2% Mg, 45.5% Ca, and 36.4% H."

Some additional tests on moisture retention were done on two soil samples, collected on the Georgia Tech campus, referred to as "Skiles soil" and "Landis soil", that have not been fully characterized so far. Table 2 contains size analyses for these soils. Coarse particles above 14 mesh were removed from later test procedures.

Table 2. Particle Size Analyses on Dried Soil Samples (As Received)

Tyler mesh size	Weight Percent		
	SRL Soil	Skiles	Landis
>14 mesh	16.1	-	-
14-20	10.0	16.63	14.91
20-30	11.1	10.70	8.70
30-40	12.8	11.70	10.23
40-50	14.5	13.37	12.45
<50	35.4	47.60	53.71

a. Measurement of Moisture Profiles.

To obtain proper correlation between retained moisture and migration observed it was important to measure moisture profiles with some accuracy. The literature contains a variety of tests, such as conductivity tests, shrinkage tests, neutron back-scatter, chemical interactions and others that are primarily suitable for in site measurements in the field (17, 18, 20, 21). However, for laboratory systems it was decided that a simple weight-loss on drying procedure would be most appropriate and easiest to use.

Tests were conducted on samples of varied but known water content, on small columns and on samples taken from the "test box", which will

be described later. Check runs to establish consistency of results were highly satisfactory; Figure 2 illustrates duplicate runs for sand samples of known water content.

Sampling in the test box was done by driving a hollow tube, about 2.5 cm I.D., vertically into the moist sand bed. Best results were obtained by a procedure in which liquid nitrogen was poured around the sampling tube while it was located in the test bed, to freeze the sand momentarily. The sampler could then be withdrawn with the sand intact inside and the sand column sectioned and measured. Figures 3 and 4 are representative of a number of moisture profiles obtained by flooding the sand bed, then lowering the water level some distance below the surface and allowing the water content in the sand to reach an equilibrium distribution. It is evident that the nominal water level does not represent an abrupt step change in moisture distribution; rather, there is a small but significant drying of the surface level layer.

Finally, a number of moisture profiles for drained soil samples were obtained. The soil was packed into thin plastic columns which were saturated with water and left standing. The columns were then allowed to drain for 24 hours, sectioned and tested for moisture content. Figure 5 shows the retained moisture profiles for "Skiles" and "Landis" soils. Results for SRL soils will be commented on later.

To facilitate larger-scale migration tests in a permeable medium a "test box" was constructed which is illustrated in Figure 6. The box was constructed of marine grade plywood; Figure 7 shows the main dimensions. The inner box, 13" x 13" I.D. contains the test medium, resting on a gravel layer and fine-mesh grid support for easy drainage.

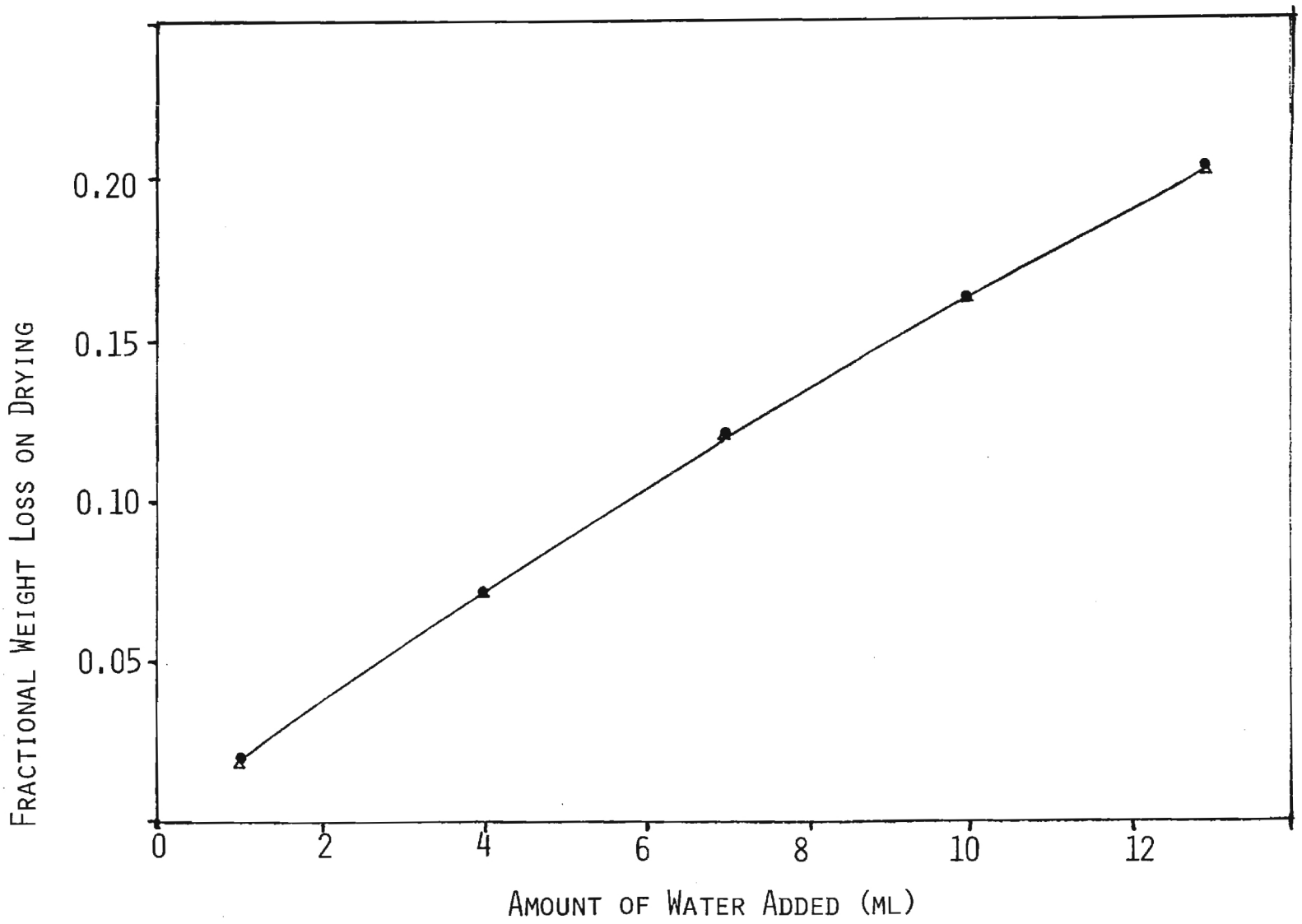


Figure 2. Moisture determination in sand samples (duplicates).

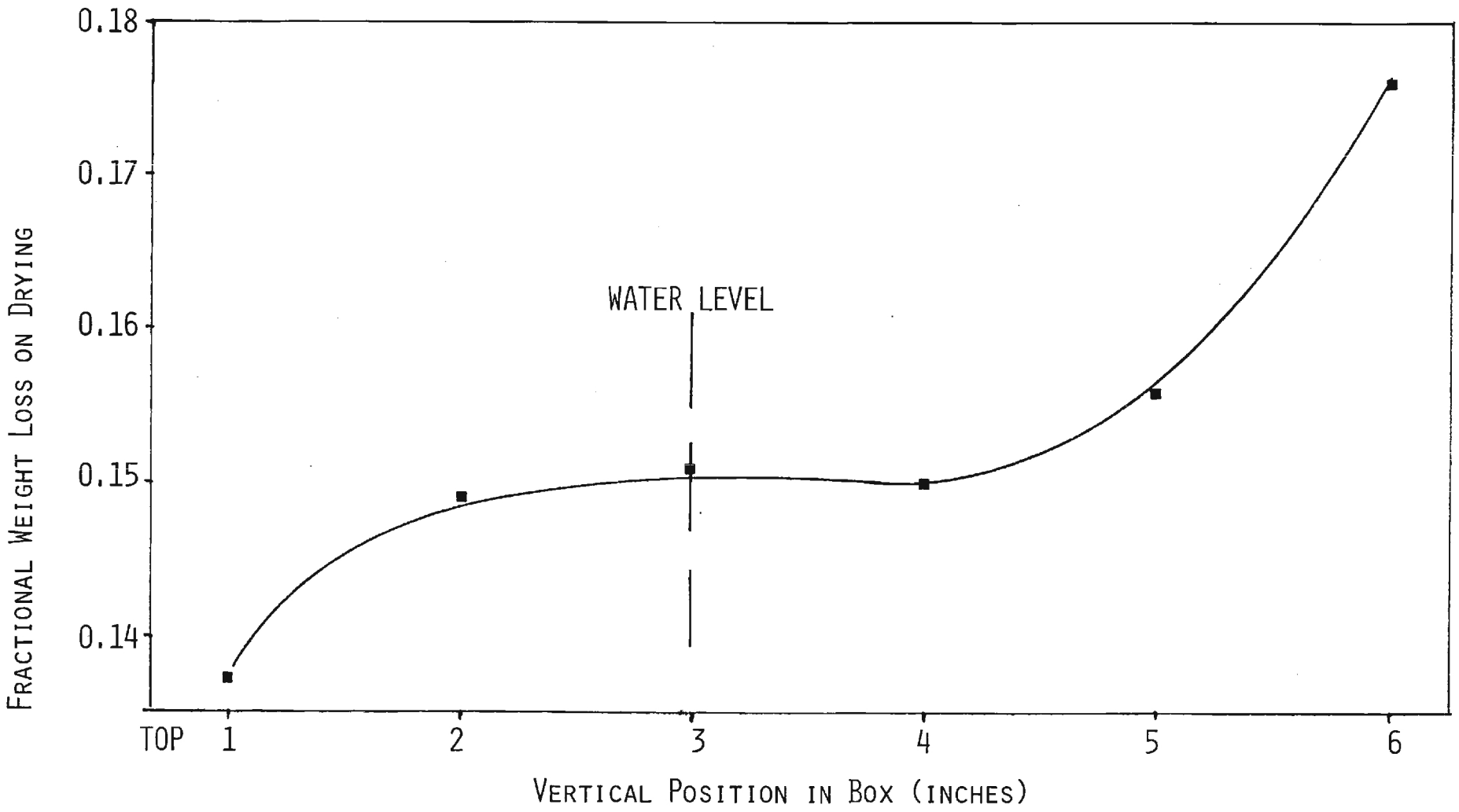


FIGURE 3. MOISTURE PROFILE NEAR WATER LEVEL IN SAND BED - 18 HR DELAY

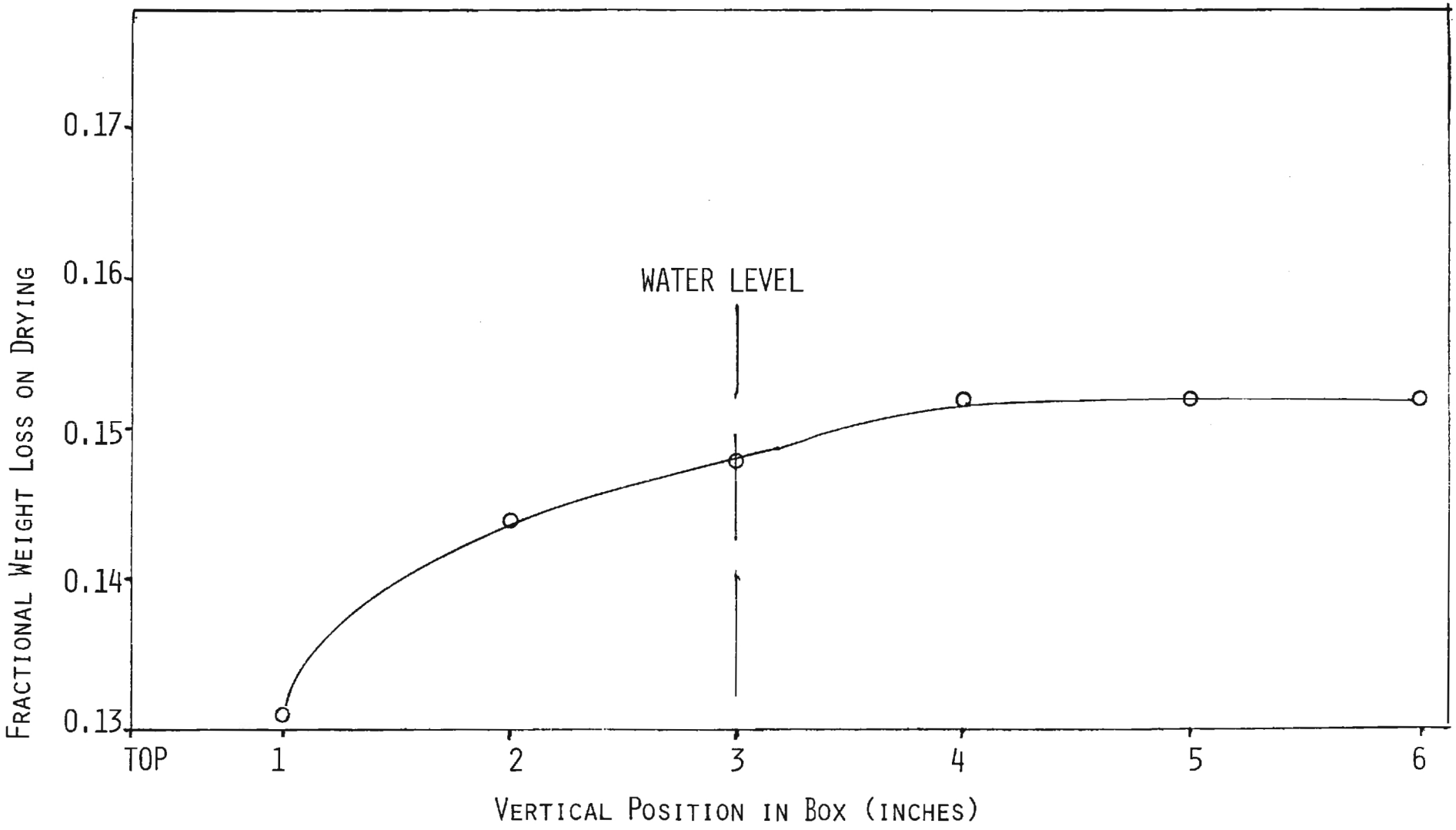


FIGURE 4. MOISTURE PROFILE NEAR WATER LEVEL IN SAND BED - 25 HR DELAY

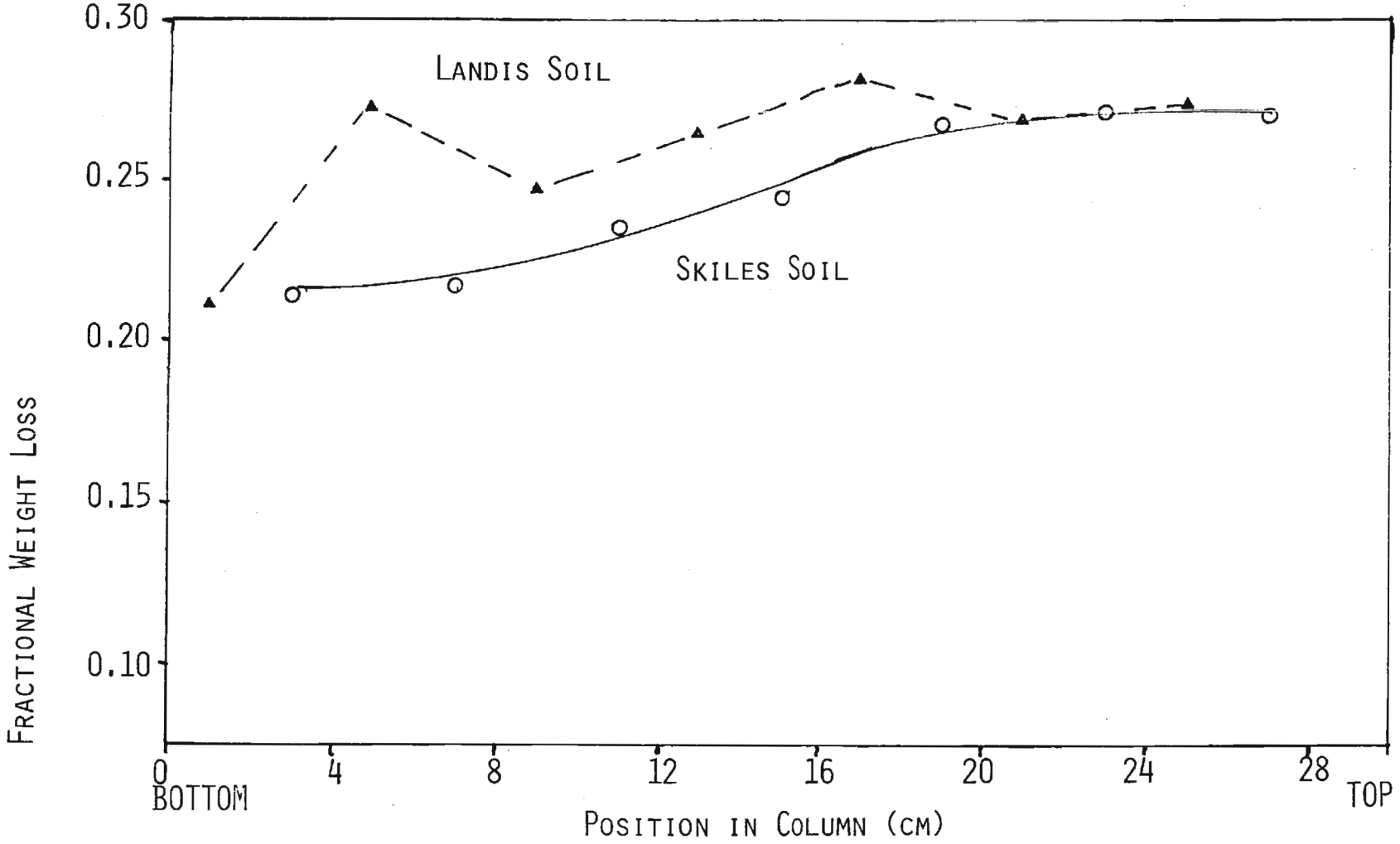
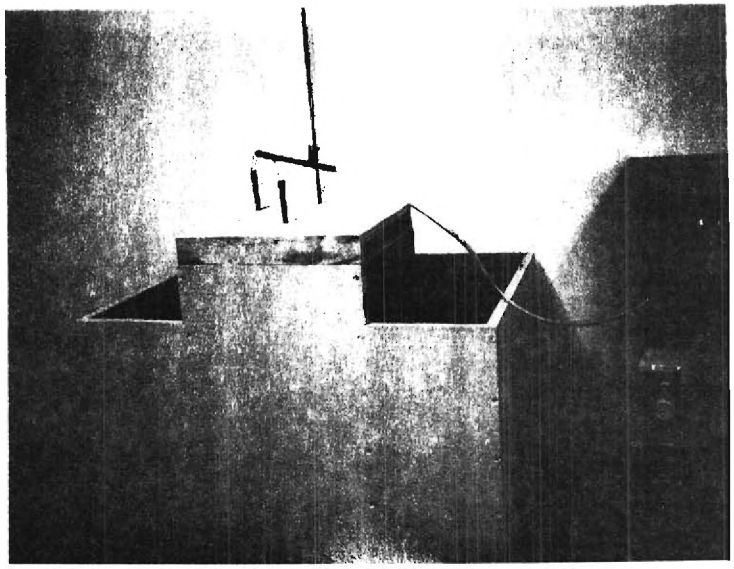


FIGURE 5. MOISTURE PROFILES FOR DRAINED SOIL COLUMNS.



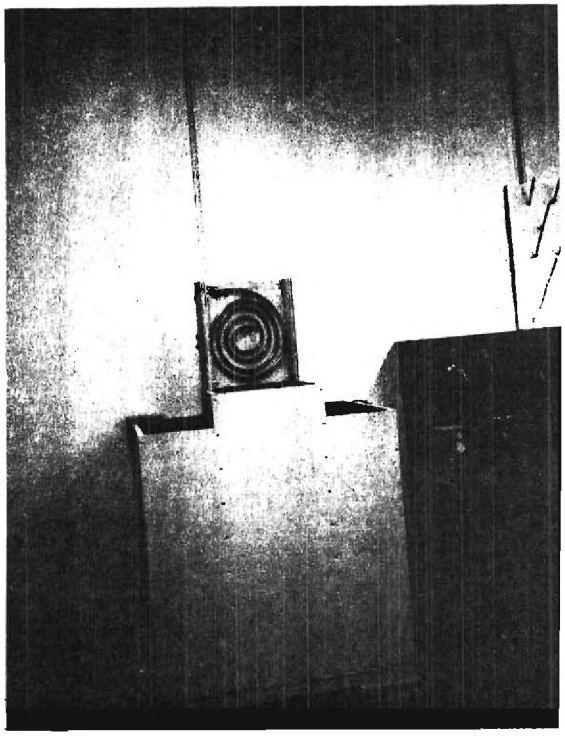


Figure 6. - Views of the Test Box

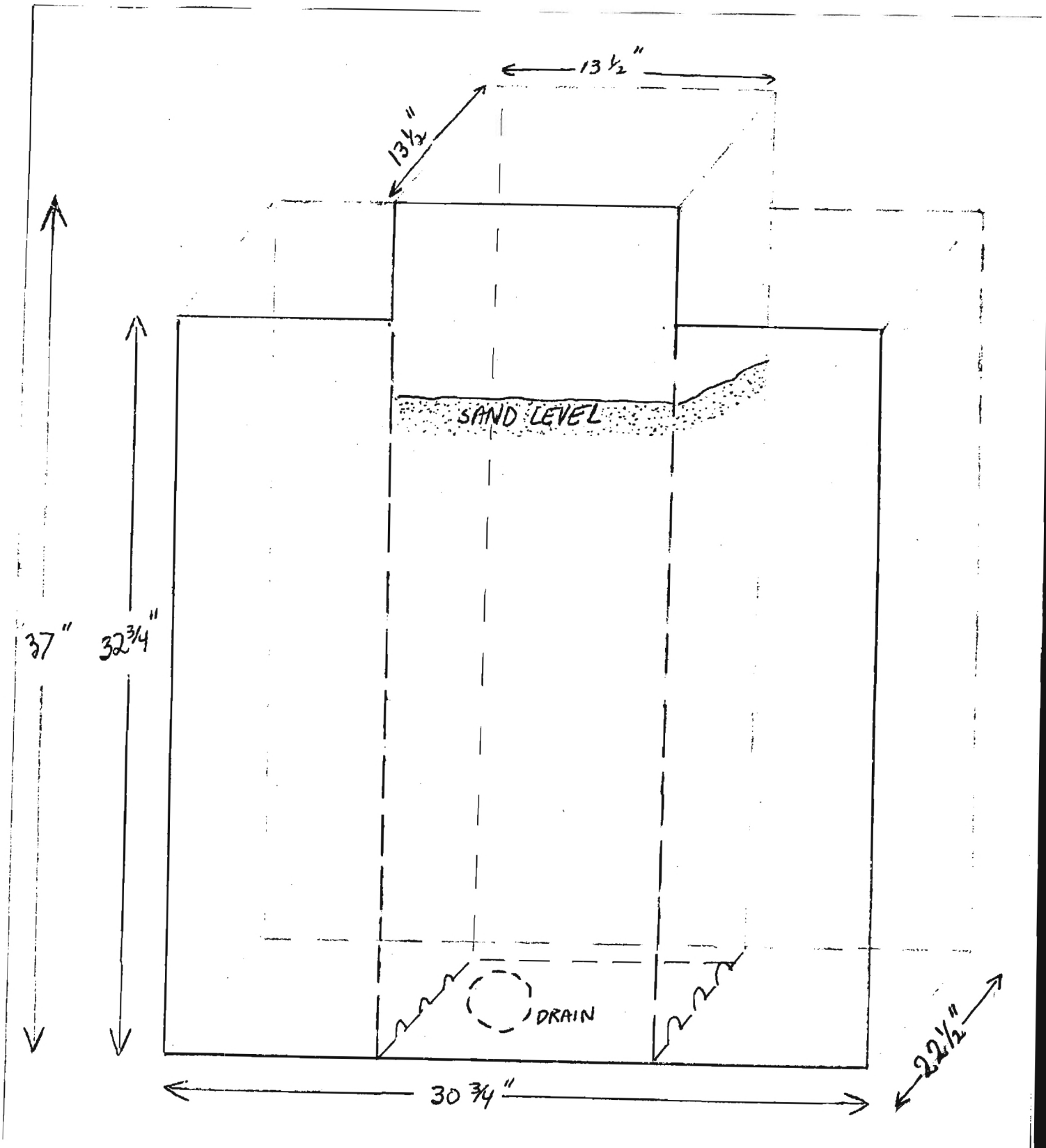


Figure 7. - Diagram of Test Box

The outer portion of the box serves as a water reservoir whose level can be raised or lowered as needed. The interior bottom of the box was carved with copper and the inner and outer boxes connect through a number of small openings near the bottom. The box has been tested for tightness and employed in a number of preliminary runs, some of them using dye solutions.

To facilitate uniform distribution of water across the bed under low flow conditions a perforated spiral tube was attached to the lid of the box as shown in Figure 8. Water can be injected by means of a pulsed-drive pump, so that water is squirted periodically onto the bed surface at an adjustable rate. At a setting of 20 full strokes per minute a flow rate through the box of 43 ml/min was obtained. This was estimated to correspond to a rainfall of 1.13 inch/hr (2.87 cm/hr).

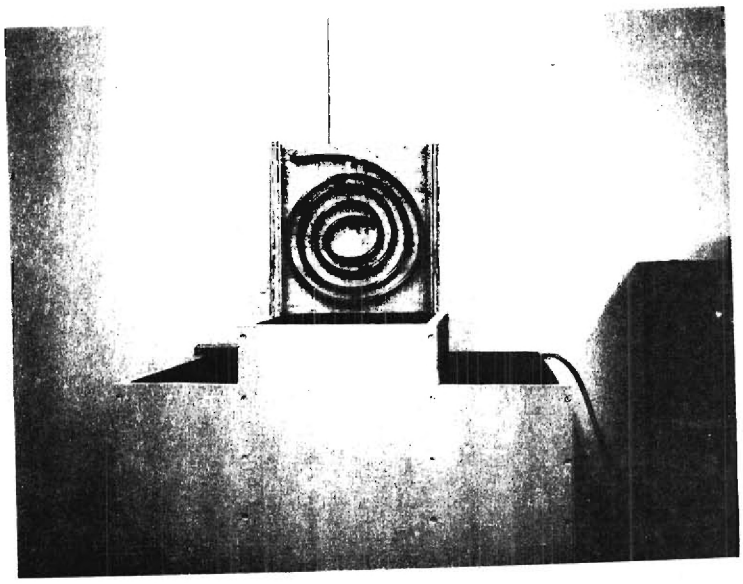


Figure 8. - View of Spray Injector for Test Box

b. Migration of dissolved ions in soil columns.

One of the central concerns of this project is the mobility of dissolved ions in moist soil materials. To investigate this, plastic tubes, 15 cm long, 1.25 cm I.D. were filled with the soil material. Cesium-137 was used as the radioactive tracer throughout. After filling the column with distilled, deionized or equilibrated water it was either left saturated or allowed to drain. The movement of the tracer could be observed by scanning the column externally, using a collimated proportional counter (Figure 9); sometimes, especially with a short column, scanning a sealed column in a horizontal position was more convenient. For a more detailed profile, the bed material was extruded at the end of a run in equal amounts or column portions. Each segment was then counted on a scintillation detector.

Most of these tests were done with columns filled with SRL soil which was found to be nearly impermeable. After saturating the column and standing, 1 ml of Cs-137 solution was added. A series of distribution curves were obtained with the columns saturated or drained, with single and multiple tracer injections, and these are illustrated in the following figures. Tests were run in triplicate and showed a high degree of consistency. Figure 10 shows the distribution for a fully saturated column, measured after allowing 26 hr. for the Cs-137 to move into the column. As Figure 10 shows the activity moved into the column as a sharply peaked band with a peak 4.5 cm from the bed surface. Allowing a longer migration time, 261 hr., broadened the band somewhat but moved the peak only a little, to 5 cm from the top (Figure 11). Later addition of 1 cc to the column did not appear to shift the peak,

Figure 9. - Counting System for Scanning a Vertical Column.

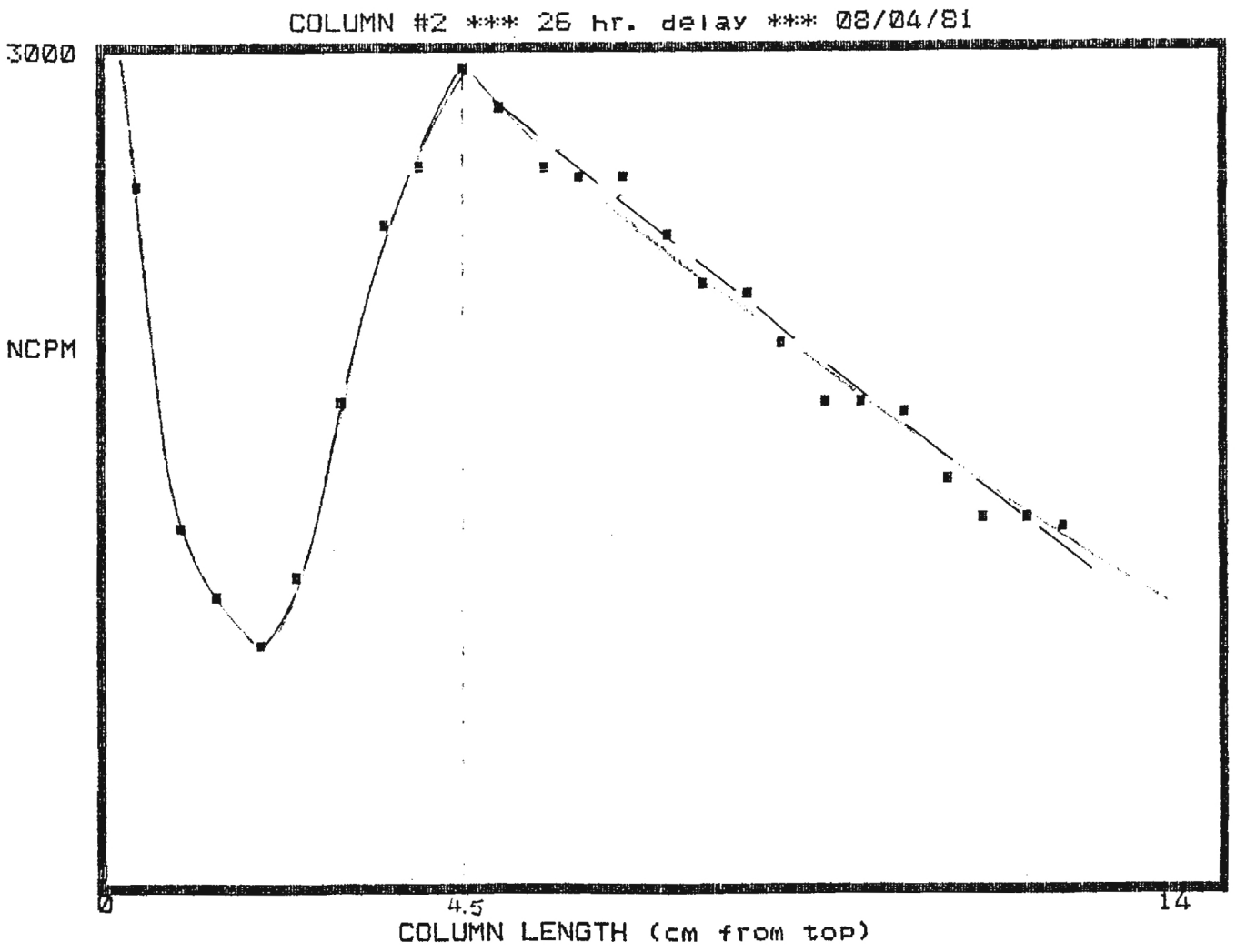


Figure 10. - Migration of Cesium into Saturated Soil Column - SRL Soil. 26 hr. Delay.

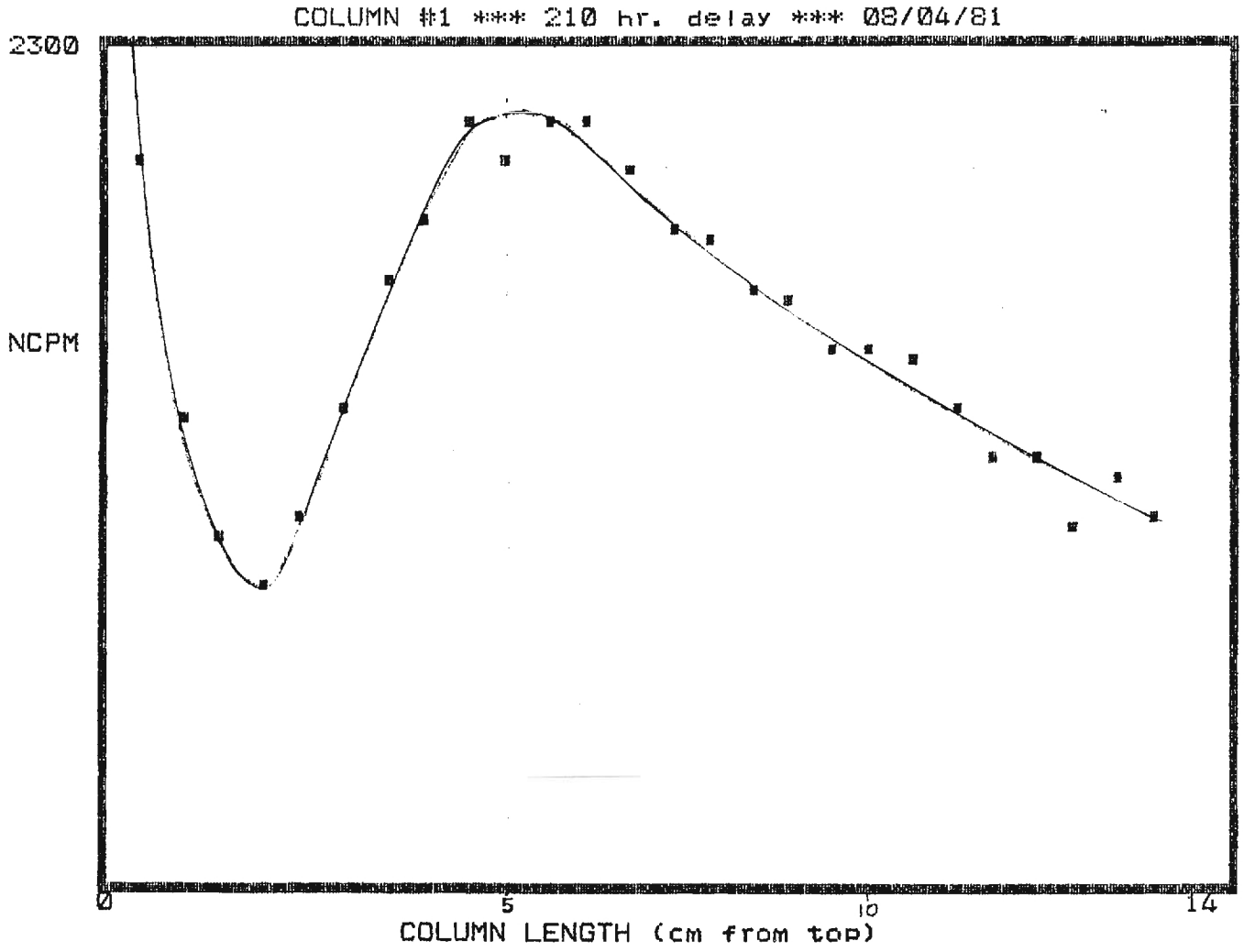


Figure 11. - Migration of Cesium into Saturated Soil Column - SRL Soil. 210 hr. Delay.

that is, remobilize the adsorbed cesium. The main effect of longer standing times was a diffusional broadening of the peak in both directions, as shown in Figure 12. The flow rate through the soil column with some standing head of water was measured to be 0.5 ml/hr.

In the next series of tests, the column was allowed to drain for 24 hr. before the tracer solution was added. As Figure 13 shows, there was no apparent difference in the fixation of the cesium, which migrated roughly the same distance in the column as before. Adding 1 ml of water and waiting over 200 hr. did not shift that peak (Figure 14). It is not immediately obvious why the cesium peak seems to be fixed in the same position in both cases. To correlate the mobility of the sorbed ions with residual moisture, the drained column was dissected and its moisture profile determined. As Figure 15 shows, the upper dip in cesium concentration seems related to a dry region and diffusional spread is pronounced just above the retained moisture maximum in the drained column. Future tests will have to pursue this matter further, which clearly opens up a new perspective on tracer mobility in moist soil matter.

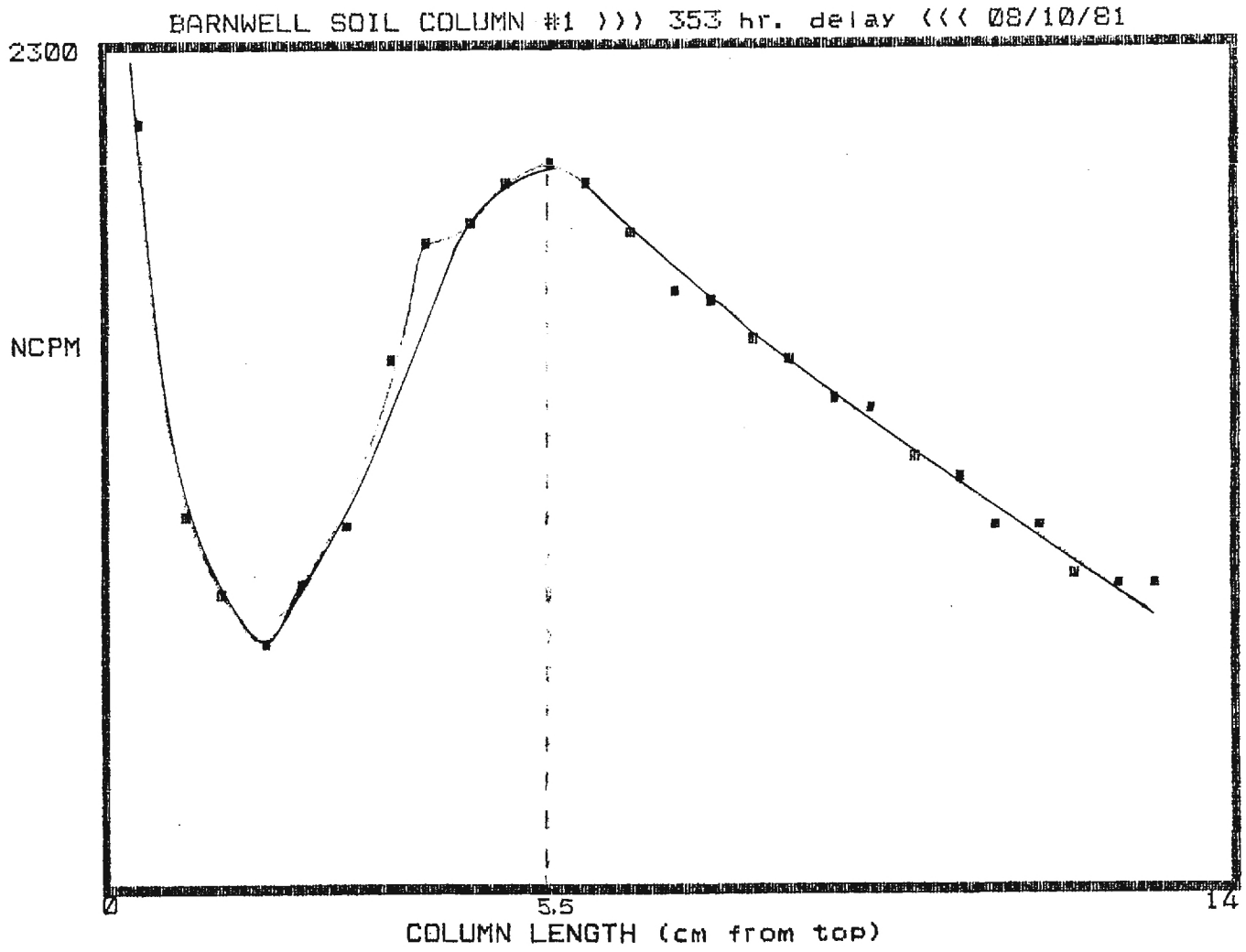


Figure 12. - Diffusional Broadening of Cs-137 Adsorption Band in Saturated Soil.

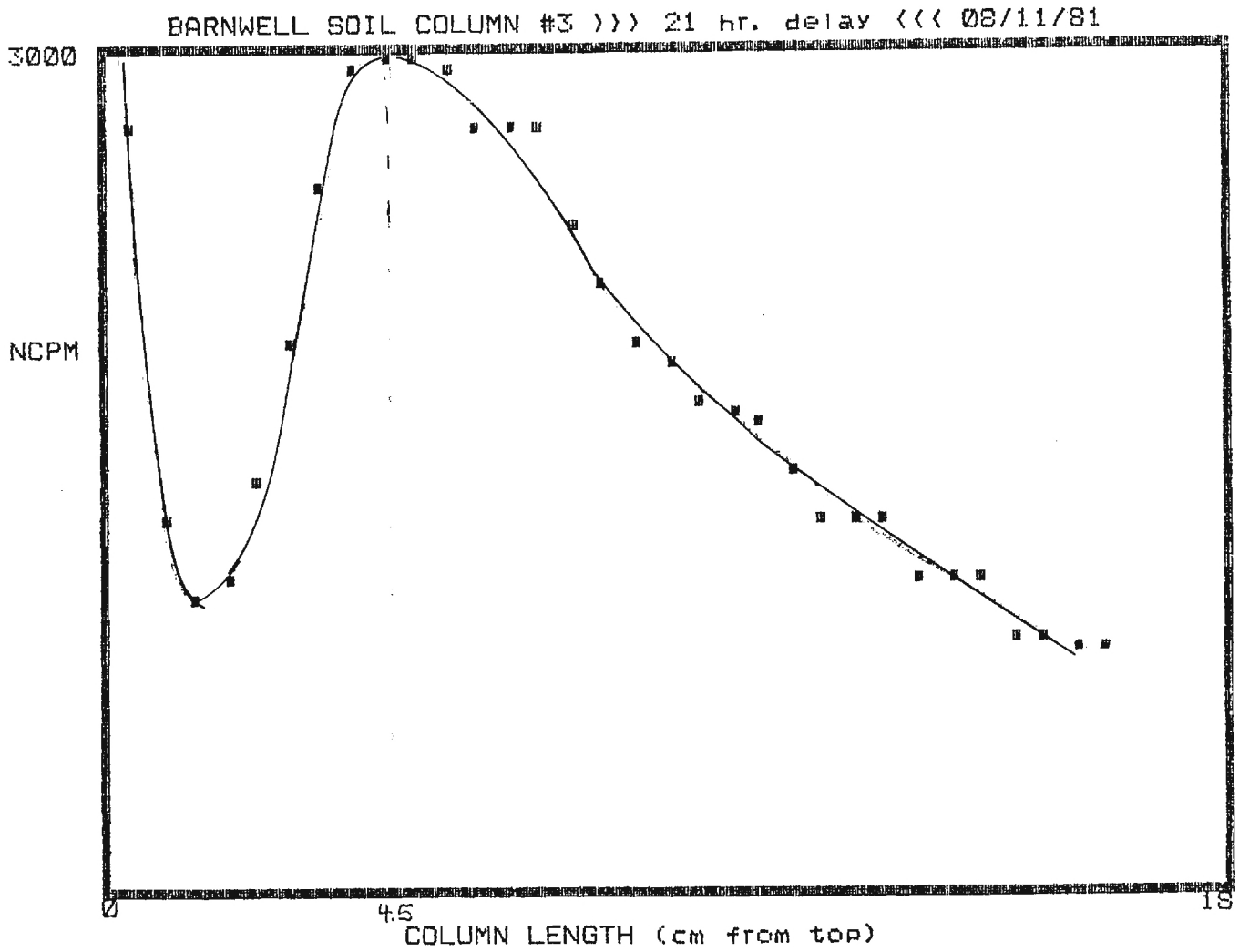


Figure 13. - Cesium Distribution in Drained Soil Column.-21 hour delay

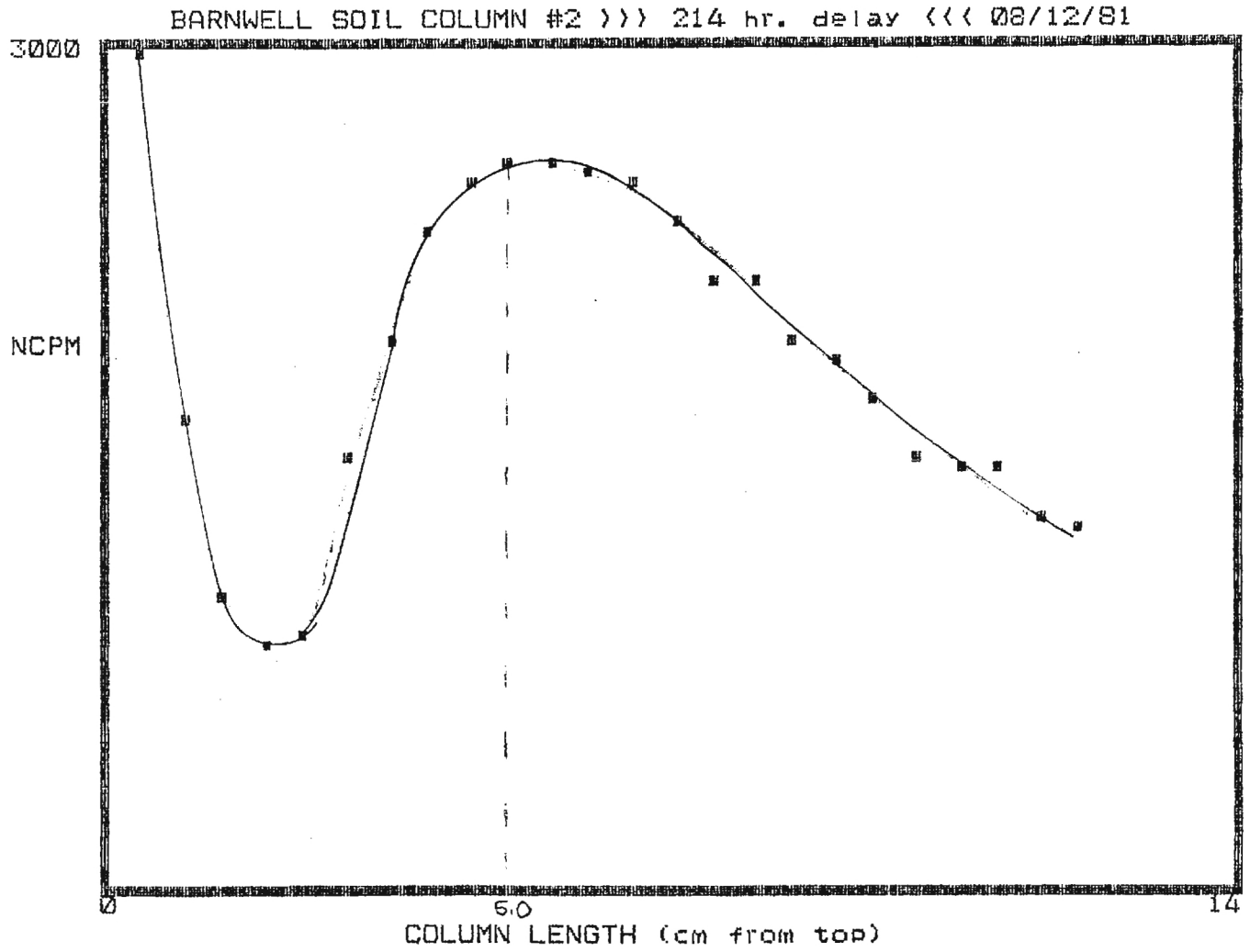


Figure 14. - Cesium Distribution in Drained Soil Column.-214 hour delay

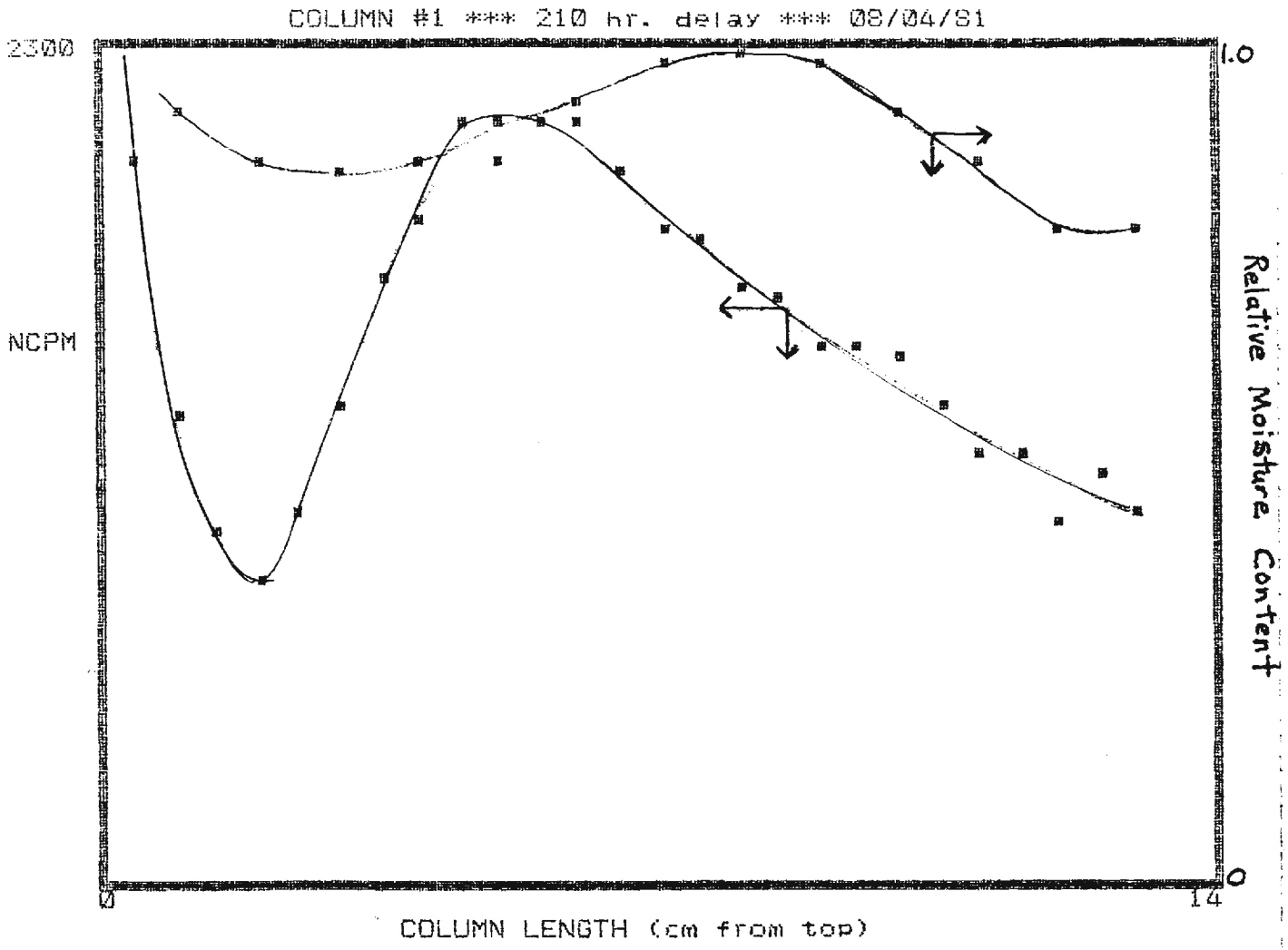


Figure 15. - Correlation of Cesium Retention and Moisture Content in Drained Soil Column.

B. Migration of Particles in Permeable Rock Columns.

Previous work has demonstrated the potential of suspended matter to serve as carriers for dissolved waste ions (13, 14). That work had shown that fine clay particles will migrate through permeable rock and soil, subject to retention and retardation effects that depend on the nature of the rock mineral surfaces and the properties of the water. Though previous work was mainly concerned with deep repositories, similar situations arise in the vadose zone, with a higher probability of naturally-occurring particulates of organic origin (10). Kaolin suspensions have been used to simulate the fine suspended matter and have been followed through columns of sand, shale, dolomite and basalt in deionized, equilibrated and saline waters (22). The suspensions were activated briefly in the Georgia Tech Research Reactor, resulting in a 15-hour sodium-24 activity which provides a convenient tracer for the particles. The movement of the particulates was recorded by determining their activity, with time, in the effluent from the test columns and, also, by dissecting the columns and measuring the retained activity along the column (14). A striking feature of some of the column tests was the occurrence of both a prompt peak in the effluent and a delayed one which was assumed to be due to some chromatographic effects, though none could be found to account for the particular delay periods.

Although the suspensions had been washed carefully and treated with H_2O_2 to remove trace organics there was always a nagging suspicion regarding the origin of the sodium impurity and whether it might still enter the solution. Tests were conducted with sodium-activated kaolin to determine what sodium, if any, was soluble and could be separated by

ion exchange resins. Table 3 compares the extent of sodium removal by different treatment methods. Treatment with KNO_3 was most effective in removal of soluble sodium.

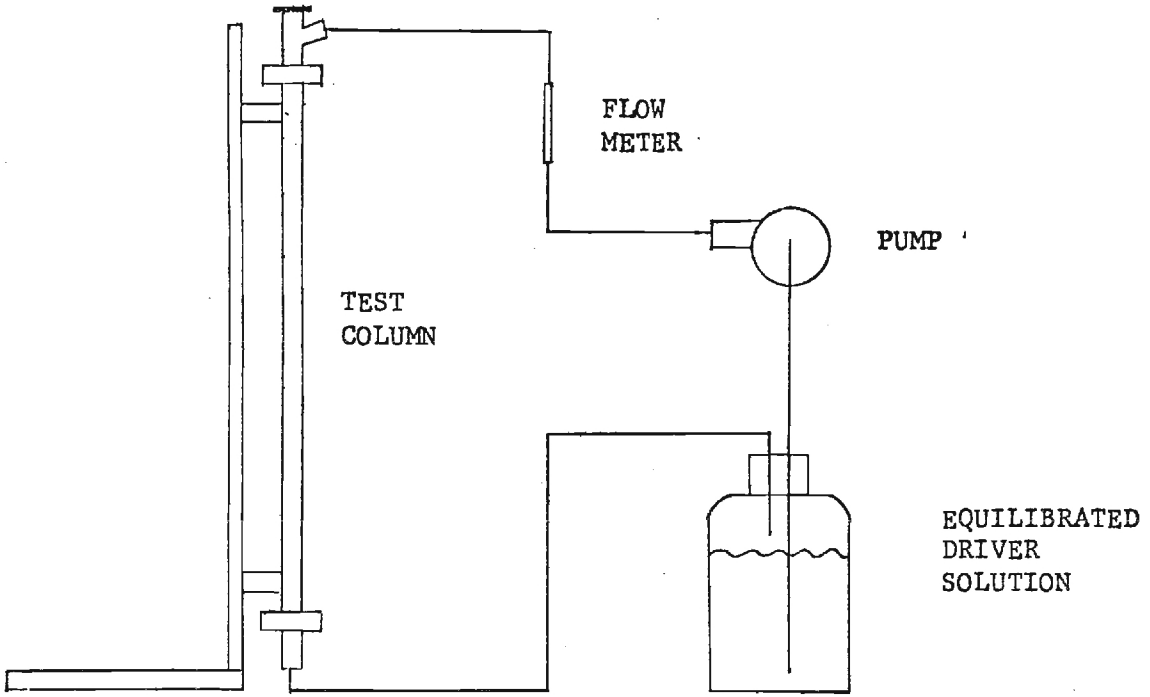
Table 3. Reduction of Soluble Sodium From Kaolin Suspension

Treatment	Activity (counts/5 min)
Filtration & decanting	111,600
KNO_3 treatment of supernate	57,424
Kaolin precipitate (untreated)	158,529
KNO_3 treated precipitate	155,217

Higher count rates for precipitates are due to change in sample geometry which was not corrected for.

To avoid any ambiguity due to the soluble Na component, a kaolin sample was activated for a longer period and the Na-24 allowed to decay. This left La-140 (40 hr.) and Sc-46 (85 days) as the main residual activities, both of them clearly structural impurities. Most of the subsequent tracer work was done with scandium-46 as the indicator.

The experimental set-up for these column tests is shown diagrammatically in Figure 16. It consists of a polycarbonate tube, 61 cm long, packed with 30-40 mesh crushed rock material, through which rock-equilibrated water is circulated, typically at a flow rate of 1 ml/min. Loading the columns to exclude any air bubbles proved to be a critical procedure; for that reason all air bubbles were first re-



Fgure 16. - Experimental Setup for Particulate Migration Tests

moved from the column, while submerged in warm water, with a squeegee. The rock material was deaerated in a slurry by boiling, then poured into the column while the column was mounted in a vibrator. After filling, the column top was affixed with a screen to hold the fill material in position. The kaolin suspension was injected by syringe into the circulating stream directly above the top of the column, usually after the equilibrated water had circulated through the column for about a day.

After injection, the flow rate of the driver solution flowing through the column was maintained at 1 ml/min and effluent samples were collected in poly vials in time intervals dependent on the rate of activity collected in the sample vials. At the point in the run when the activity leaving the column was at its greatest concentration the frequency of sample collection was increased to increase the number of data points obtained over this period.

The collected samples were dried under heat lamps and counted for gross gamma activity with a NaI(Tl) scintillation detector. The net counts together with the wet and dry weights of each sample were used as input data to a computer routine. This routine gives the x and y coordinates necessary to plot a graph of fraction of activity released per void volume of solution passing through the column. One void volume is the volume of liquid occupying the volume not occupied by mineral in the column. The void volume of a column can be determined by finding the difference in weight between a column filled with dry rock and a column completely filled with water and rock. For most of the test runs the void volume was of the order of 35 cc.

After collecting samples for 5 hours or more, the flow through the column was halted. The column was then dismantled and the column was sectioned into pieces approximately 2 cm in length. These sections were dried under heat lamps, weighed, and counted for gross gamma activity. The activity per unit mass (cpm/gm) was plotted against an indication of position from the top of the column (cumulative mass from top measured in grams). Most runs were run in duplicate.

Figure 17 shows a representative plot for the effluent activity emerging from a column. Note the sharp initial peak, containing the majority of particles traveling at water velocity so that they emerge at 1 void volume (VV), followed by a long tail of particles, containing only a small portion of the particulates, but which is delayed in the column over a very long period, presumably by a combination of surface-interaction and trapping effects.

The distribution of particles retained within the column is shown in Figure 18 for shale. As in previous work (14) two regions can be discerned, a narrow strip at the top where physical trapping ("filtering") prevails, and the bulk of the column, where sorption effects result in a slight, but still significant retention. It is the latter which are presumably responsible for any delay effects.

Considerable interest attaches to the nature of this delay process and it has been studied in some detail. In some materials it seems to be chromatographic in character. For example, Figure 19 shows a pronounced second peak, arising from the injection of a second tracer dose 45 min. after the first. To follow up this effect a test was run in which three tracer injections were done an hour apart; this compares with a column residence time of the order of 30 min. As Figure 20

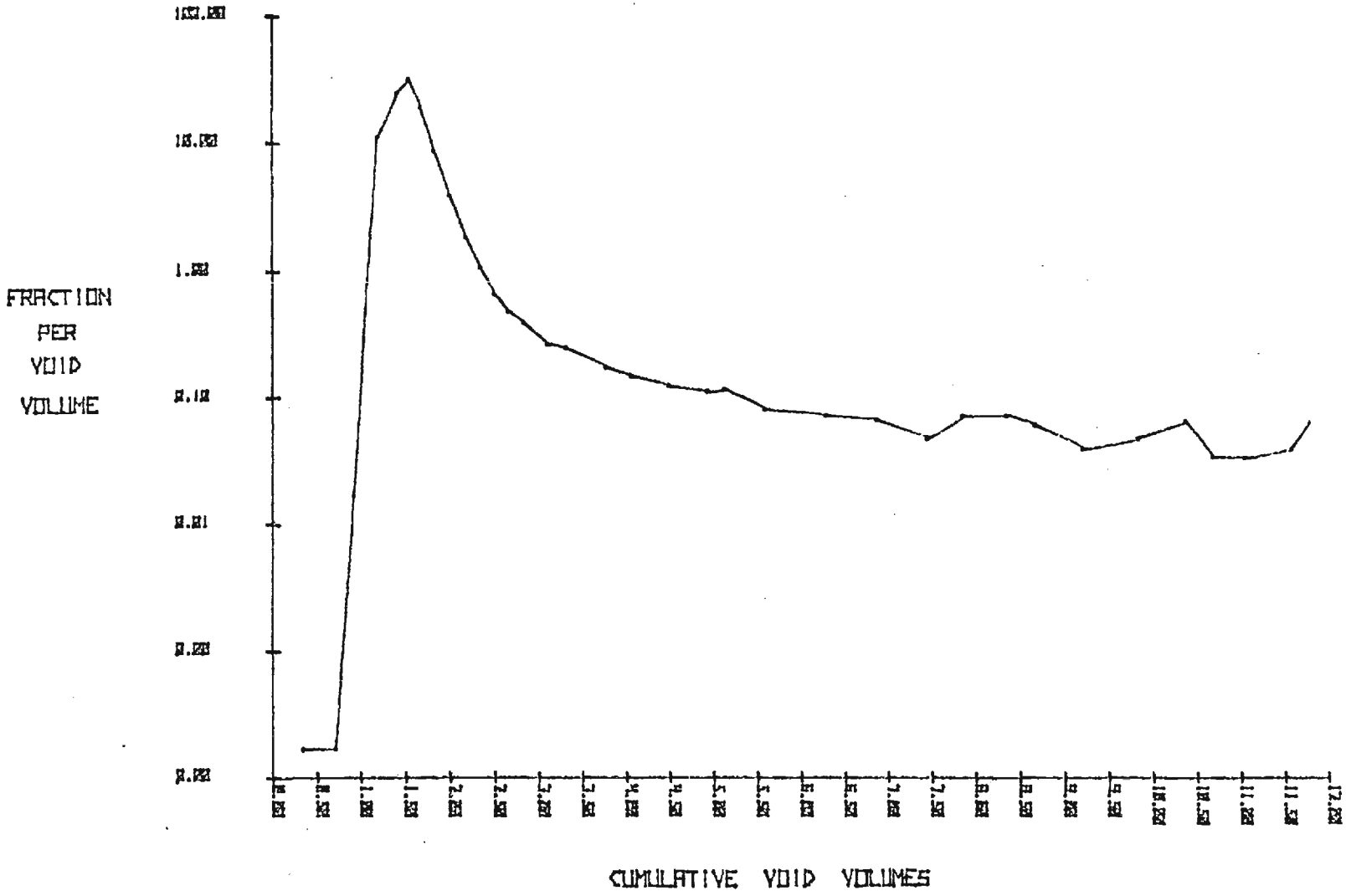


Figure 17. - Representative Graph of Activity Released from Columns

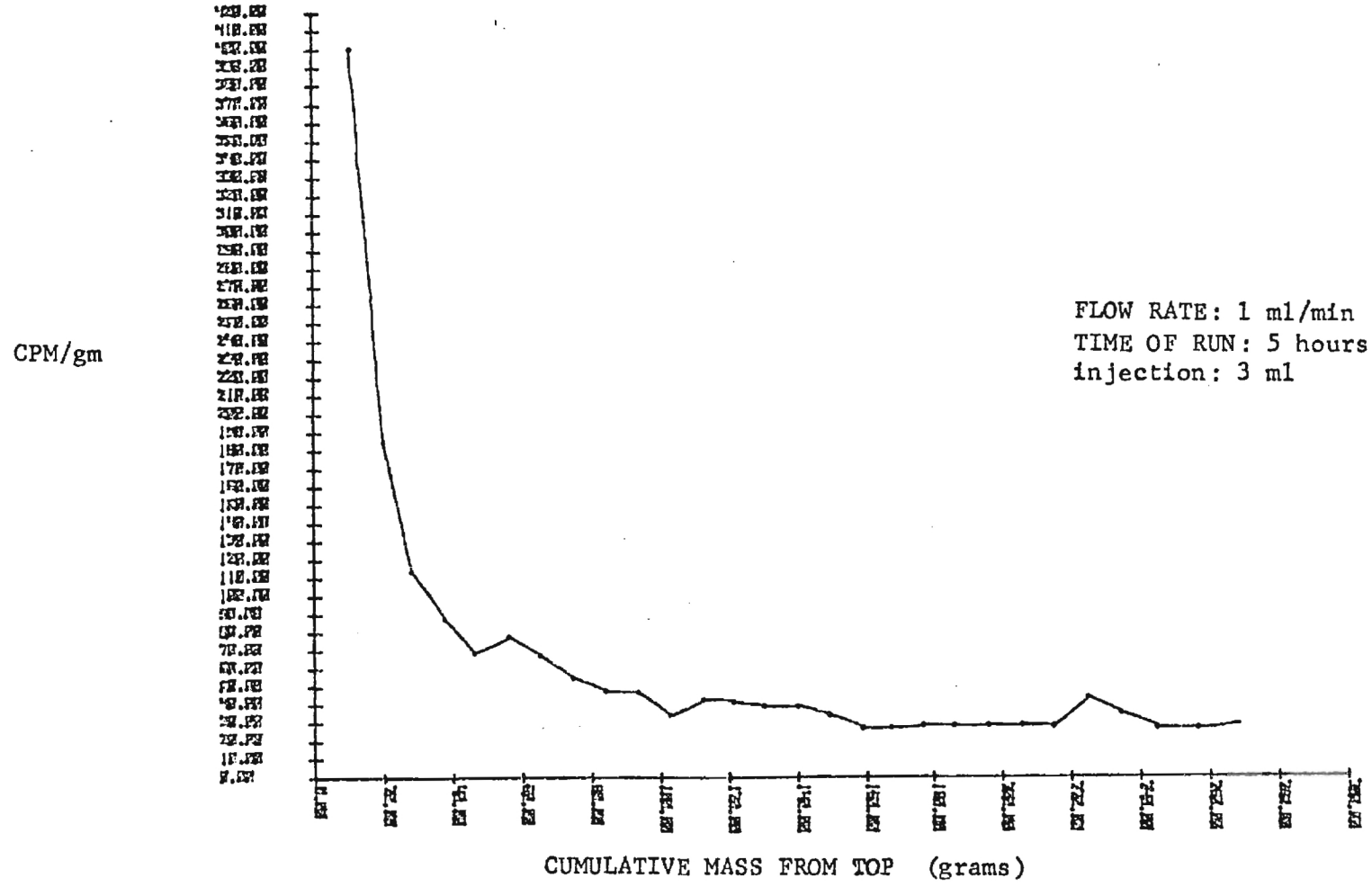


Figure 18. - Shale Column (#S81281A) Dissection

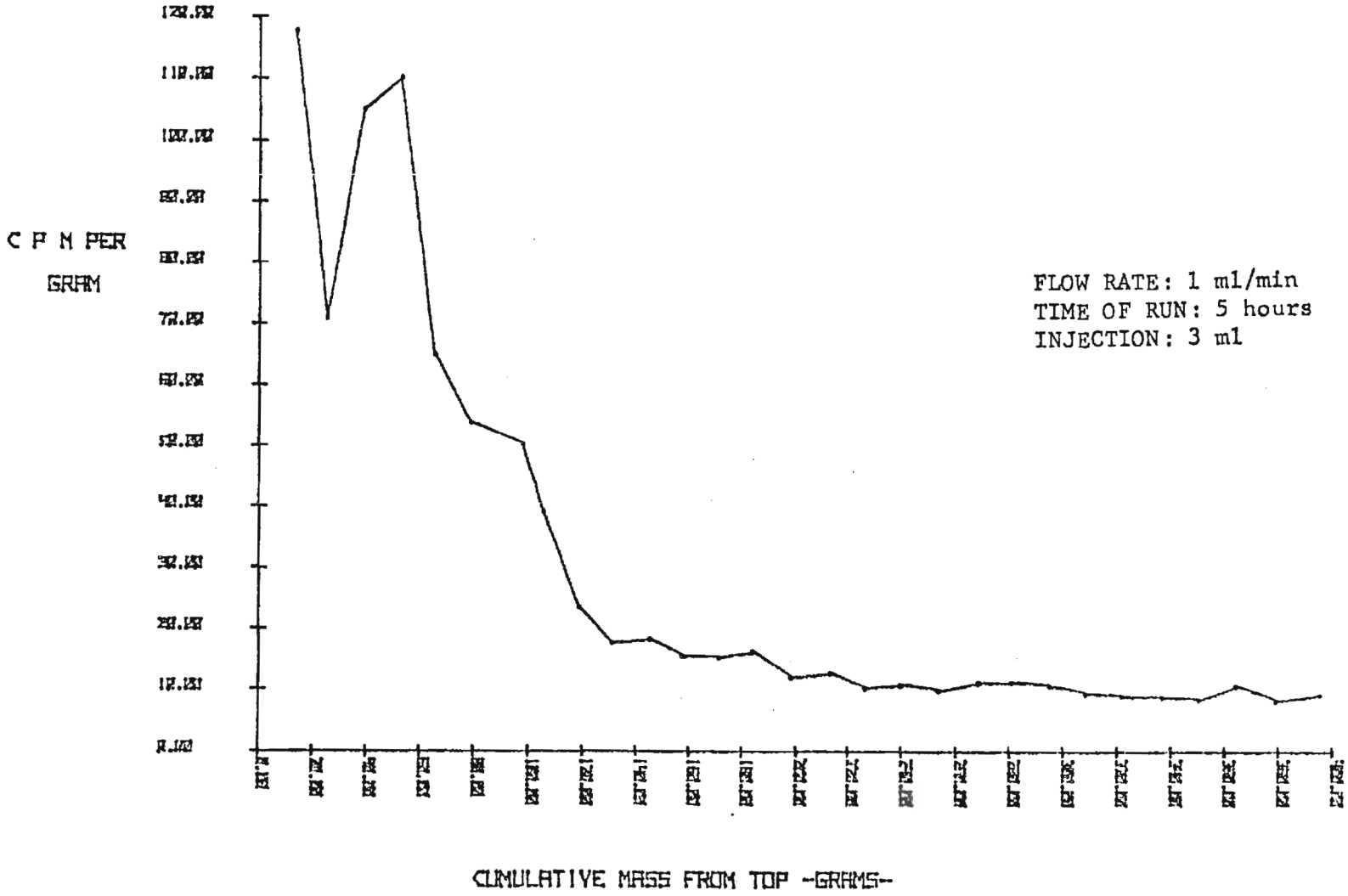


Figure 19. - Shale Column (S071081) Disection

shows, separate bands of activity did, in fact, occur along the column, though the first two merged to some extent. The bulk of the injected particles again from all three injections would have passed through the column promptly, long before flow was stopped and the column material was scanned.

Similar runs were obtained with sand and basalt. No visible delayed band was observed in sand; however, in basalt such a peak was found as seen in Figure 21. Again a significant delaying effect occurred.

To evaluate numerically the retention and sorption effects, Table 4 shows the partitioning of the particulate flow in the column. The injection conditions were not always entirely comparable; for instance the first shale run was the triple injection test. However, it is evident that 75-85% of the particulates were retained in the column, the rest appeared in the effluent. Not all of the retained activity is trapped permanently as is evident from the continued appearance in the effluent shown in Figure 17.

To compare the relative significance of fittering at the top of the column and delay sorption the filter coefficient λ' and the sorption coefficient μ' were calculated from the slopes of the distribution plots. Table 5 shows the results for the runs listed in Table 4 per gram of bed material. To convert to λ' and μ' per unit surface area, a previous determination had indicated a surface area of 10 m^2/g for the shale.

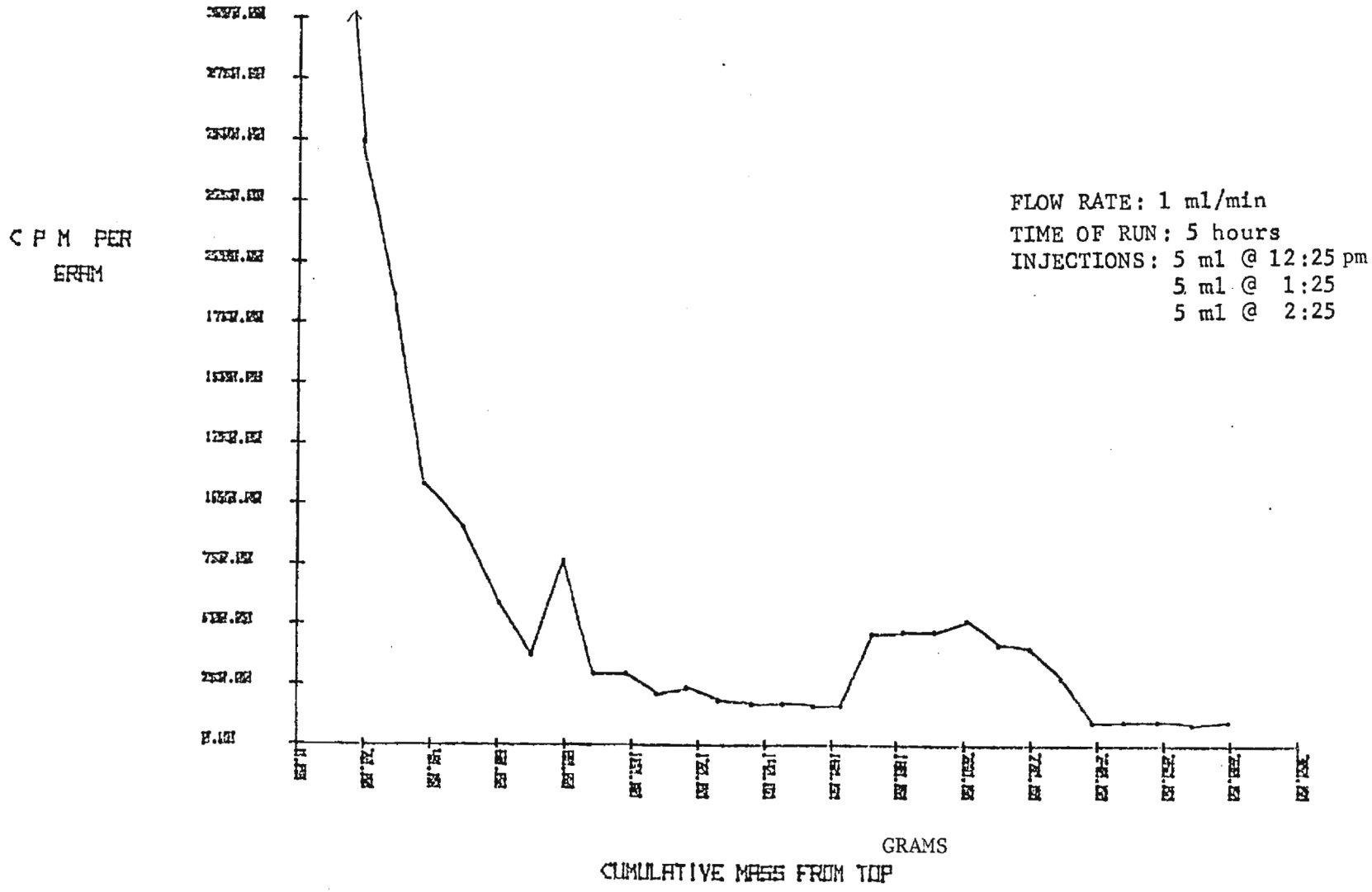


Figure 20. - Particulate Distribution on Triply-Injected Shale Column

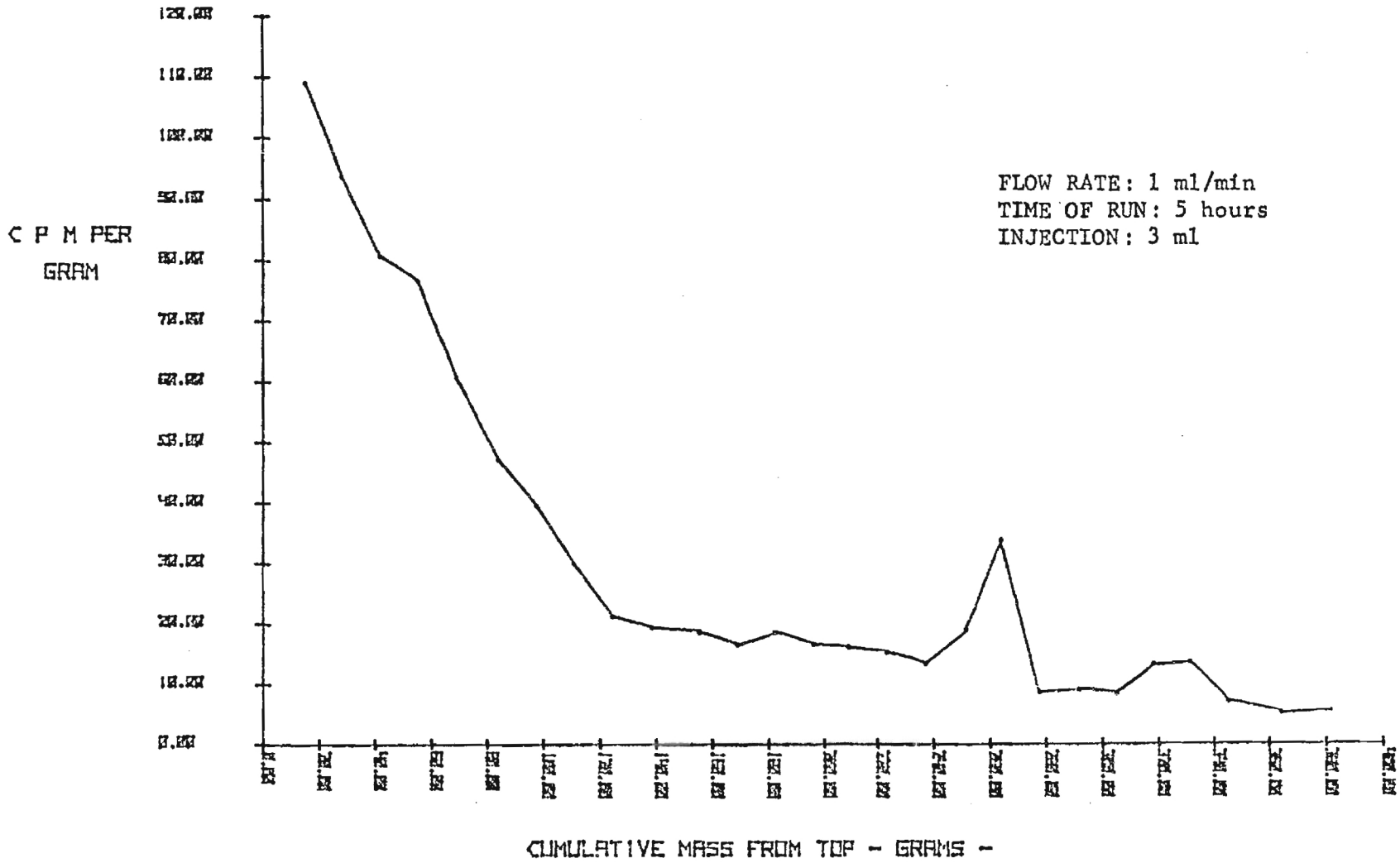


Figure 21. - Basalt Column (#B071081) Dissection

Table 4. Activity Distribution in Shale and Basalt Columns.

COLUMN	ACTIVITY IN COLUMN		ACTIVITY IN EFFLUENT	
	net CPM	% total	net CPM	% total
B071081 Basalt	8,944	84.2%	1,678	15.8%
S081981 Shale	210,046	88.1%	28,490	11.9%
S071081 Shale	9,303	83.0%	1.960	17.0%
S81281A Shale	13,102	76.9%	3,945	23.1%
S81281B Shale	12,547	76.2%	3,919	23.8%
S73181A Shale	1,507	83.5%	298	16.5%
S73181B Shale	1,425	75.6%	461	24.4%

Table 5. λ' and μ' Values for Shale and Basalt Columns Per Gram of Bed Material.

COLUMN	λ'	μ'
B071081 Basalt	-0.00729	-0.00302
S081981 Shale	-0.01176	-0.00309
S071081 Shale	-0.00923	-0.00125
S81281A Shale	-0.02155	-0.00192
S73181B Shale	-0.01988	-0.00189
AVERAGE for Shale	-0.0155	-0.0020

The water circulating in the above tests was "rock-equilibrated" water into which a small amount of kaolin was injected. In order to check if the delay effect would also occur if the kaolin suspension concentration was pre-equilibrated, tests were run with kaolin-containing water. Figure 22 shows the results of such a run for sand. No detectable difference from other runs was observed. Figures 23 and 24 present effluent plots for basalt and limestone columns, respectively, with kaolin water pretreatment, showing similar results. The large delayed activity appearing late in the basalt run is not entirely understood; that test was terminated after 7 VV had been collected and presumably this delayed activity would have decreased in time.

This test work has provided further confirmation that particulates will travel through porous media subject to various delay mechanisms and must be included in any consideration of waste migration.

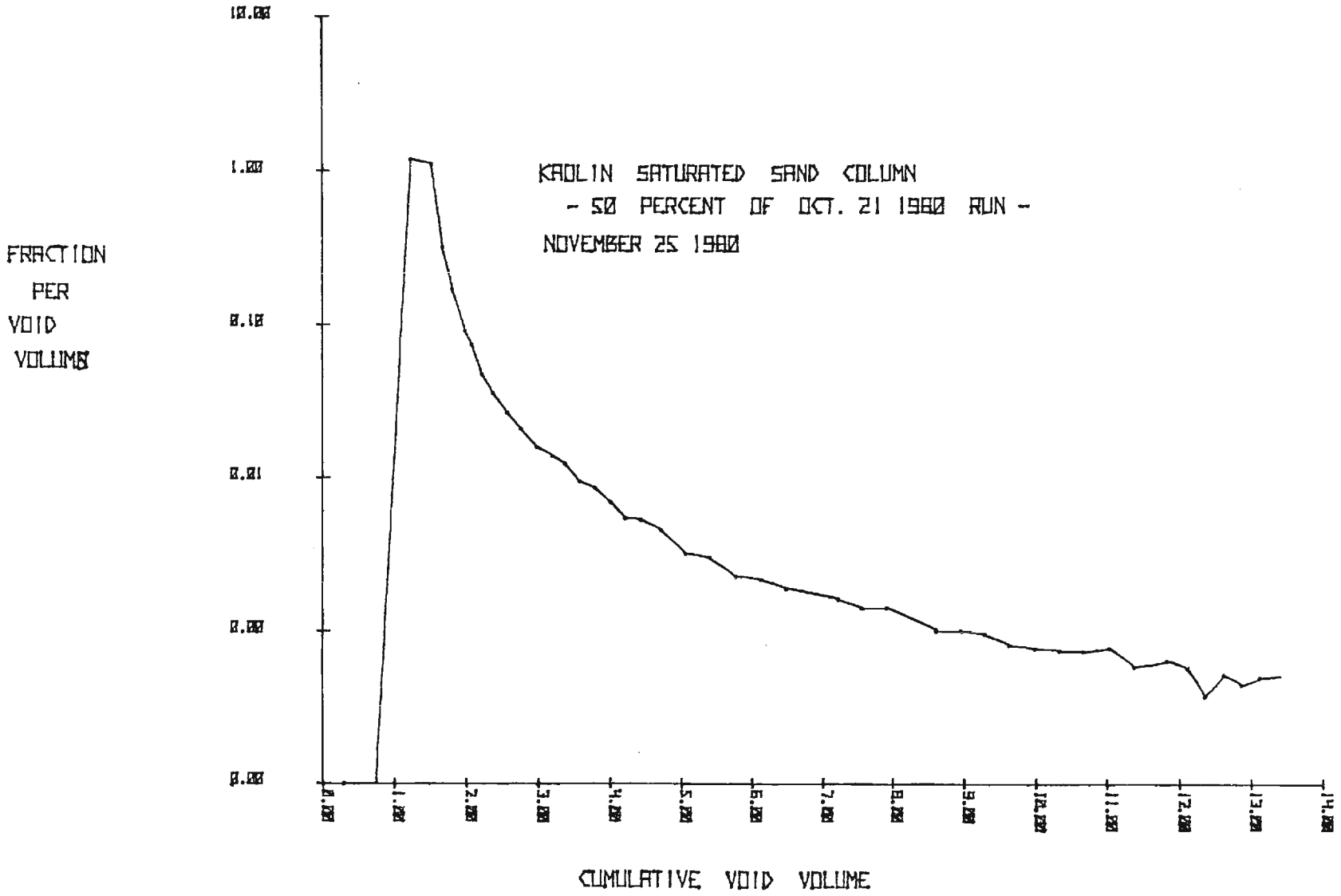


Figure 22. - Kaolin Tracer Appearance in Effluent from Sand Column Pretreated with Weak Kaolin Solution

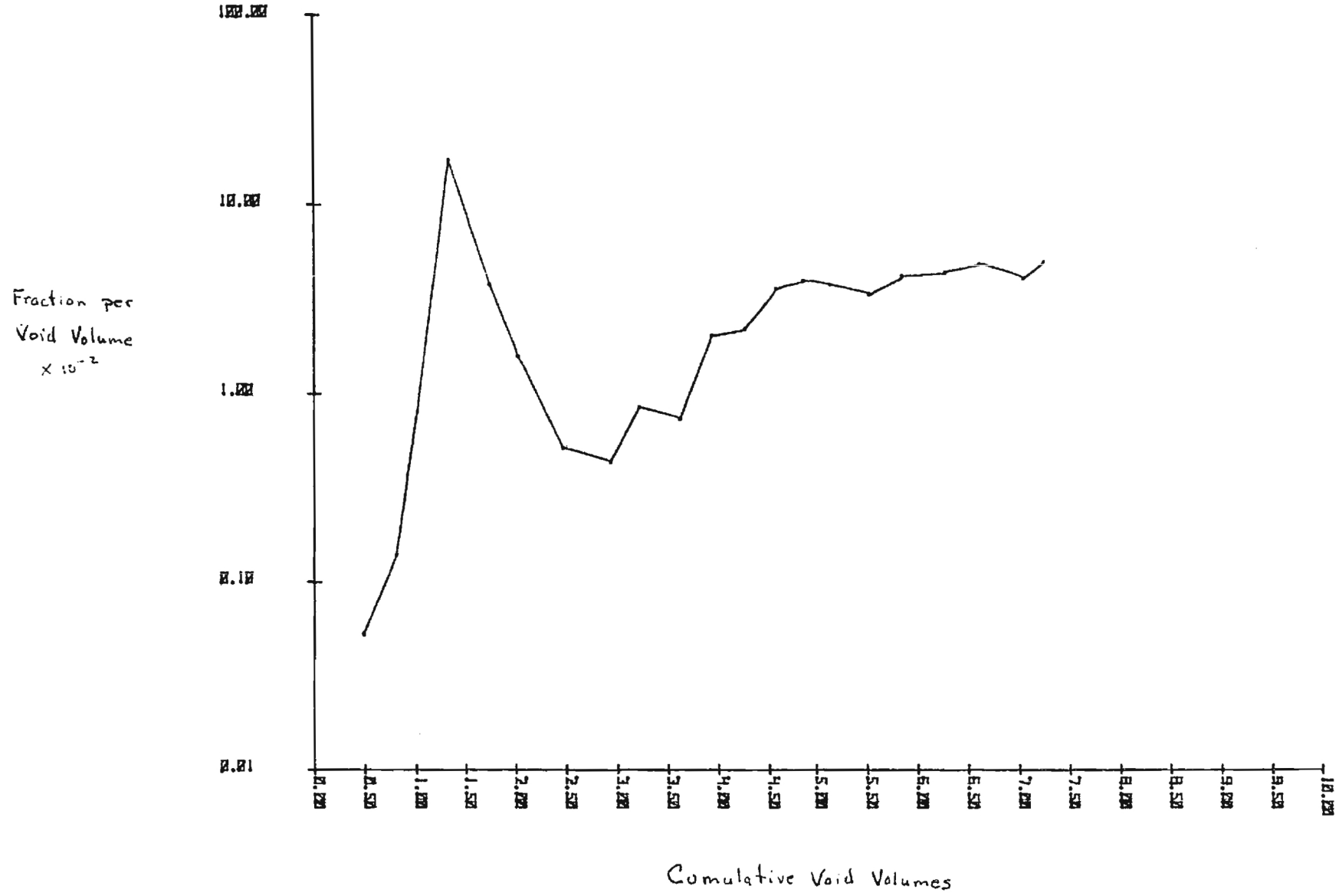


Figure 23. - Effluent Plot for Particulate Flow Through Basalt Column - Kaolin Water Equilibration

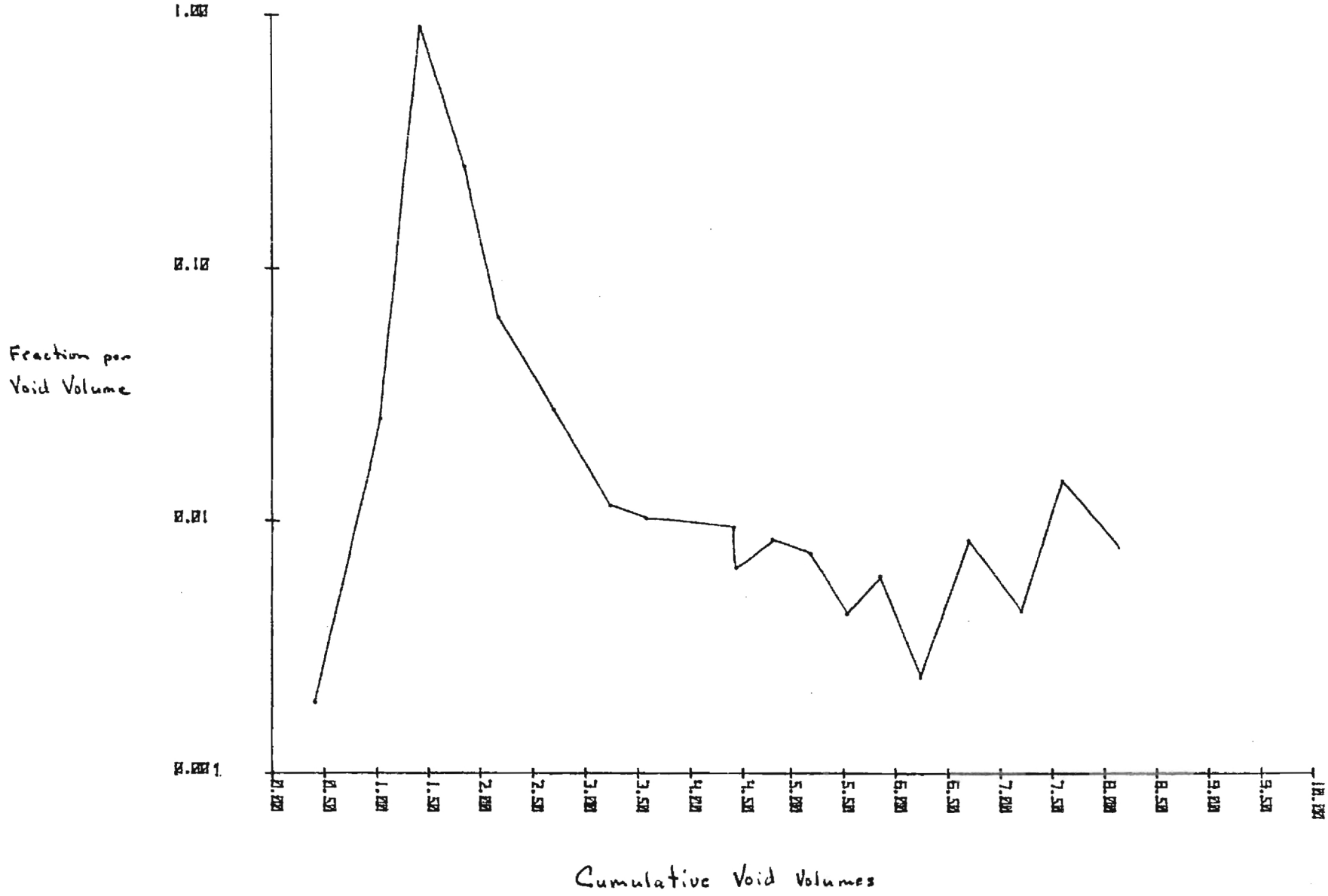


Figure 24. - Effluent Plot for Particulate Flow Through Limestone Column - Kaolin Water Pretreatment

Waste Remobilization and Effects of Complexants

In repositories near the surface and even in some deeper ground waters there may be an appreciable concentration of complexing agents, humic acids and a variety of organic materials. Table 6, taken from an ONWI Progress Report, shows some of the ions found in groundwater in a generic granite. In radioactive disposal sites chelates from chemical processing may occur in leach waters, as seen in Table 7, also taken from an ONWI Progress Report (ONWI-9(2), 1980), for chelates like NTA and EDTA found in water samples at the Maxey Flats disposal site. Other reagents, such as phosphates, may arise from fertilizers contained in surface run-off water.

To study the consequences of the presence of such agents, bench tests have been performed on the change in surface adsorption on various rock materials for dissolved tracer ions and suspended matter when complexing agents are present in ground water (Figure 25). Additional experiments were performed to study any desorption of retained tracers when such reagents are added to the surrounding water.

As in the work described in the previous section, rock samples employed included limestone, shale, basalt and dolomite samples, whose provenance is shown in Table 8, and sand and kaolin as previously described. Measurements were conducted to determine the partitioning of radioactive tracer elements between kaolin and rock surfaces in distilled or equilibrated water. Subsequently, similar measurements were done with sodium or ammonium phosphate present. Finally the change

in tracer absorption was determined when phosphates or chelates were added to the solution.

Table 6. Ground-Water Composition of a Generic Granite

Component	Range, mg/ℓ
Ca^{2+}	20-60
Na^{+}	10-100
Mg^{2+}	5-30
Fe_{tot}	1-20
Fe^{2+}	0.5-15
K^{+}	1-5
Mn^{2+}	0.1-0.5
HCO_3^{-}	60-400
CI^{-}	5-100
SO_4^{2-}	1-40
NO_3^{-}	0.1-2
PO_4^{3-}	0.01-0.6
F^{-}	0.5-3
HS^{-}	<0.1-5
CO_2	0-25
SiO_2	5-40
NH_4	0.1-0.4
NO_2	<0.01-0.1
O_2	<0.01-0.07

TABLE 7. ^{238}Pu AND CHELATE CONTENTS OF THE MAXEY FLATS TRENCH LEACHATES

Sample	Dissolved (<0.05 μm) ^{238}Pu, pCi/liter[1]	NTA	EDTA, ppm	DTPA
A	3,540	possible[2]	0.10	ND[3]
D	51	***	***	***
N	718	***	***	***
O	976	ND	0.45	ND
R	8,060	possible	0.15	ND
DD	7,378	possible	0.10 (approx.)	ND
FF	2,568	***	***	***
GG	1,838	***	***	***
II	486	possible	0.10 (approx.)	ND
JJ	14,100	possible	yes[4]	ND
MM	622	possible	0.06 (approx.)	ND
NN	7,460	possible	0.60 (approx.)	ND
OO	3,730	***	***	***

*** = Recovery of CDTA standard is very poor due to interference from sample matrix. Quantitative analysis will be attempted using a different derivatization procedure.

[1]All ^{238}Pu analysis were performed by the U.S. Geological Survey in Denver.

[2]Peak with appropriate retention time was observed, but identity needs to be confirmed by mass spectrometry.

[3]ND = below detection limits.

[4]Sample JJ definitely contains EDTA but amount cannot be quantified because of poor CDTA yields.

Table 8. Rocks Utilized in the Present Studies (from Ref. 14)

Oolitic Limestone	Indiana	Wards Natural Science Establish. Cat. No. 47W4670
Marble (Limestone)	Tate, Georgia	Georgia Marble Co.
Sentinel Gap Basalt	Washington State Highway 243 Road Outcrop between Beverly and Mattawa, WA	Pacific Northwest Laboratory, L.L. Ames
Conasauga Shale	Core Well No. OWI-OR-8 depth 16 to 100 ft.	Oak Ridge National Lab, L.R. Dole
Magenta Dolomite, Rustler Formation	Roadcut along N.M. Highway 31 near entrance to IMC mine Sec 1, T22S, R29E	Sandia Laboratories, D.W. Powers
Culebra Dolomite, Rustler Formation	Roadcut along N.M. Highway 62/180 about 7 miles south of Carlsbad Airport, Sec 4, T24S, R26E	Sandia Laboratories, D.W. Powers

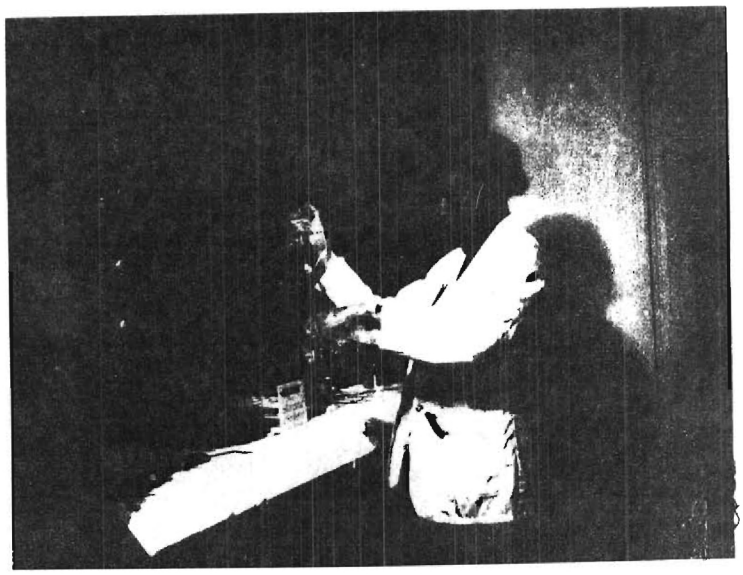


Figure 25. - Laboratory Tests on Effects of Phosphates on Tracer Adsorption on Rocks

A. Three-Component Sorption Tests.

These experiments involved adsorption on either shale, basalt or limestone (25-40 mesh) in the presence of kaolin suspension. Radiotracers used were Np-235 and Tc-95 m. The procedure consists of adding 100 λ of tracer solution, 7.5 ml of a 0.65 mg/cc kaolin suspension to 1.0 g of pulverized rock in 7.5 ml of rock-equilibrated water. The pH was adjusted with 0.1 M NaOH if needed. 24 hours was usually allowed to elapse before separating the constituents by decanting the supernatant liquid and precipitating the kaolin for counting. Half of the clear solution was removed for counting, the other half was put back into the rock solution for washing it. The rock material was washed from the test tubes and counted and the empty tubes were counted to record wall absorption losses. Variations on this basic procedure were applied as appropriate. Some of the results obtained are tabulated below; adsorption coefficients are expressed as K_d in ml/g.

a. Adsorption of Tc-95 m on Shale and Kaolin. Table 9.

Two quantities of shale, 0.05 and 0.25 g at pH9 and 8.8, respectively. The pH values result from limited dissolution of rock material during the equilibration period. As will be seen in other tests, true steady state in some cases is rarely reached even after a week's contact.

Table 9. Adsorption of Tc-95m on Shale.
Temp. 20°C.

Mass of Shale	Tracer	Initial pH	Final pH	K_d Values	
				Shale	Kaolin
0.050g	Tc-95m	9.90	9.00	3.19	55.2
0.050	Tc-95m	9.88	9.02	3.22	53.7
0.250	Tc-95m	9.88	8.80	2.19	56.5
0.250	Tc-95m	9.97	8.67	2.32	59.2

b. Adsorption of Np-235 on Basalt and Kaolin.

Base case, for varying amounts of basalt, pH between 9 and 10 - Table 10.

It is evident that gram for gram the fine kaolin suspension adsorbs a large proportion of the total activity. The variation in the basalt values also illustrate why K_a values, per unit surface area, are more useful for rock samples, than K_d values which presuppose a volume effect for sorption.

The next test repeated the Np-235 with ammonium phosphate or sulfate added to the equilibrated solution - Table 11.

Although the pH was not greatly different, it is obvious that the small amount of phosphate added greatly increased both K_d values, especially for the kaolin. The addition of sulfate was relatively insignificant, as expected, and the NH_4^+ ion was not the active agent.

c. Adsorption of Tc-95m on Basalt and Kaolin.

Base case, for varying amounts of basalt, pH $\sim$ 9.1-94 - Table 12.

Results resemble those for neptunium.

The next test was the base case at low pH, $\sim$ 2.2-2.3 - Table 13.

Table 14 presents Tc-95m adsorption on basalt + kaolin with phosphate additives and ammonium sulfate. In this case the phosphate did not modify adsorption on basalt at all and it reduced it somewhat for kaolin.

Table 10. Adsorption of Np-235 on Basalt + Kaolin

Mass of Basalt (g)	Initial pH	Final pH	K_d (ml/g) Basalt	Kaolin
1,500	9.45	8.15	2.35	707
1,500	9.34	8.00	2.58	759
0.750	9.04	8.57	2.73	728
0.750	9.05	8.75	2.68	856
0.500	9.45	8.40	3.65	922
0.500	9.34	8.02	3.58	813
0.250	9.40	8.56	3.72	605
0.250	9.36	8.48	4.62	587
0.050	9.44	8.47	8.37	888
0.050	9.07	8.60	5.16	609
0.050	9.10	8.40	1.56	673

Table 11. Effect of Additives on Np-235 Sorption on Basalt + Kaolin

Mass of Basalt (g)	Additive (0.00378M)	Initial pH	Final pH	K_d(ml/g) Basalt	Kaolin
0.750*	$(NH_4)_2HPO_4$	9.48	9.40	21.9	48,300
0.750*	"	9.45	9.30	9.3	61,600
0.750	"	9.48	9.29	29.0	133,000
0.750	"	9.45	9.29	14.9	72,700
0.500	"	9.33	9.07	28.4	65,000
0.500	"	9.31	9.08	100	345,500
0.250	"	9.32	9.16	34.9	58,000
0.250	"	9.35	9.09	27.7	71,400
0.250	$(NH_4)_2SO_4$	9.28	9.20	8.98	528
0.250	"	9.32	9.26	9.76	494
0.050	"	9.32	9.30	14.2	551
0.050	"	9.30	9.20	14.0	495

*Salt was added during separation for better recovery of particulates.

Table 12. Adsorption of Tc-95m on Basalt + Kaolin (Distilled Water)

Mass of Basalt (g)	Initial pH	Final pH	K_d (ml/g) Basalt	Kaolin
0.050	9.25	8.70	1.68	238
0.050	9.20	8.80	1.20	145
0.250	9.40	8.35	0.617	158
0.250	9.25	8.30	0.618	174
0.500	9.20	8.10	1.19	183
0.500	9.10	8.09	1.16	209
0.750	9.13	8.10	0.845	145
0.750	9.10	8.05	1.81	185

Table 13. Adsorption of Tc-95m on Basalt + Kaolin at Low pH

Mass of Basalt (g)	Initial pH	Final pH	K_d(ml/g) Basalt	Kaolin
0.050	2.30	2.58	2.10	97.3
0.050	2.25	2.48	1.82	88.5
0.250	2.24	2.54	0.794	95.7
0.250	2.23	2.56	3.70	147
0.500	2.17	2.66	1.50	116
0.500	2.17	2.66	2.63	150
0.750	2.19	2.70	1.68	129
0.750	2.17	2.72	3.00	165

Table 14. Adsorption of Tc-95m on Basalt + Kaolin in the Presence of Phosphates

Mass of Basalt (g)	Additive (0.00378M)	Initial pH	Final pH	K_d(ml/g) Basalt	K_d(ml/g) Kaolin
0.050	$(NH_4)_2HPO_4$	9.20	9.18	2.28	92.4
0.050	"	9.16	9.09	2.33	86.6
0.250	"	9.17	9.08	1.10	95.8
0.250	"	9.20	9.07	1.12	93.0
0.500	"	9.27	9.12	0.920	92.9
0.500	"	9.26	9.03	0.898	94.8
0.750	"	9.23	9.03	0.835	93.3
0.750	"	9.22	9.04	0.839	94.0
0.050	$(NH_4)_2SO_4$	9.17	9.02	1.22	58.5
0.050	"	9.13	9.02	1.22	71.7
0.250	"	9.13	9.01	0.598	70.2
0.250	"	9.13	9.01	0.607	71.3
0.050	$(NH_4)_2HPO_4$	8.17	7.95	1.37	86.7
0.050	"	8.16	7.90	1.71	91.2
0.250	"	8.16	7.92	1.03	104
0.250	"	8.16	7.92	0.83	86.5
0.050	Na_3PO_4	11.66	11.29	1.41	84.0
0.050	"	11.68	11.33	1.18	89.0
0.250	"	11.70	11.34	0.676	84.0
0.250	"	11.70	11.34	0.494	88.1
0.050	"	9.55	8.66	1.52	96.1
0.050	"	9.46	8.60	1.37	91.3
0.250	"	9.50	8.55	0.635	95.6
0.250	"	9.55	8.58	0.664	88.0

d. Adsorption of Tc-95m on Limestone.

A series of runs were done with oolitic limestone (25-40 mesh) in the same fashion as for basalt - Table 15.

K_d values came out similar to basalt.

e. Adsorption of Tc-95m on sand.

A series of runs were conducted to obtain baseline data for sand. Both K_d and K_a were calculated - Table 16.

B. Adsorption and Desorption in Equilibrated Water.

A series of tests were conducted in water that had long been equilibrated and others that were reaching equilibrium while tested. After a sufficient time was judged to have elapsed, a complexing reagent was added and the partition between rock and water was remeasured. A critical factor of importance may be whether the phosphate or chelate is already in the water at the time it enters the repository and leaching occurs, or whether the chelate appears after the dissolved ion has interacted with the surrounding rock. As Figure 26 shows, in some cases there was a dramatic change in the distribution of radiotracer, in other cases it made relatively little difference. Some of these tests will be summarized in the following sections.

Table 15. Adsorption of Tc-95m on Limestone + Kaolin

Mass of Limestone (g)	Initial pH	Final pH	K_d(ml/g) Limestone	K_d(ml/g) Kaolin
0.050	9.20	8.34	1.97	131
0.050	9.18	8.31	2.28	125
0.250	9.37	8.35	1.15	124
0.250	9.40	8.50	1.10	107
0.500	9.28	8.32	1.04	115
0.500	9.34	8.38	0.986	115
0.750	9.32	8.30	0.977	118
0.750	9.30	8.28	0.991	121

Table 16. Adsorption of Tc-95m on Sand + Kaolin: pH 9

Mass of Sand (g)	K_d(basalt) (ml/g)	K_a(Basalt) (ml/m^2)	K_d(Kaolin) (ml/g)
0.50	0.744	0.039	247
0.50	0.912	0.048	160
0.50	0.71	0.037	146
0.50	0.80	0.044	-
1.0	0.70	0.036	153
1.0	0.76	0.040	167
1.0	0.66	0.035	186
1.0	0.64	0.034	168

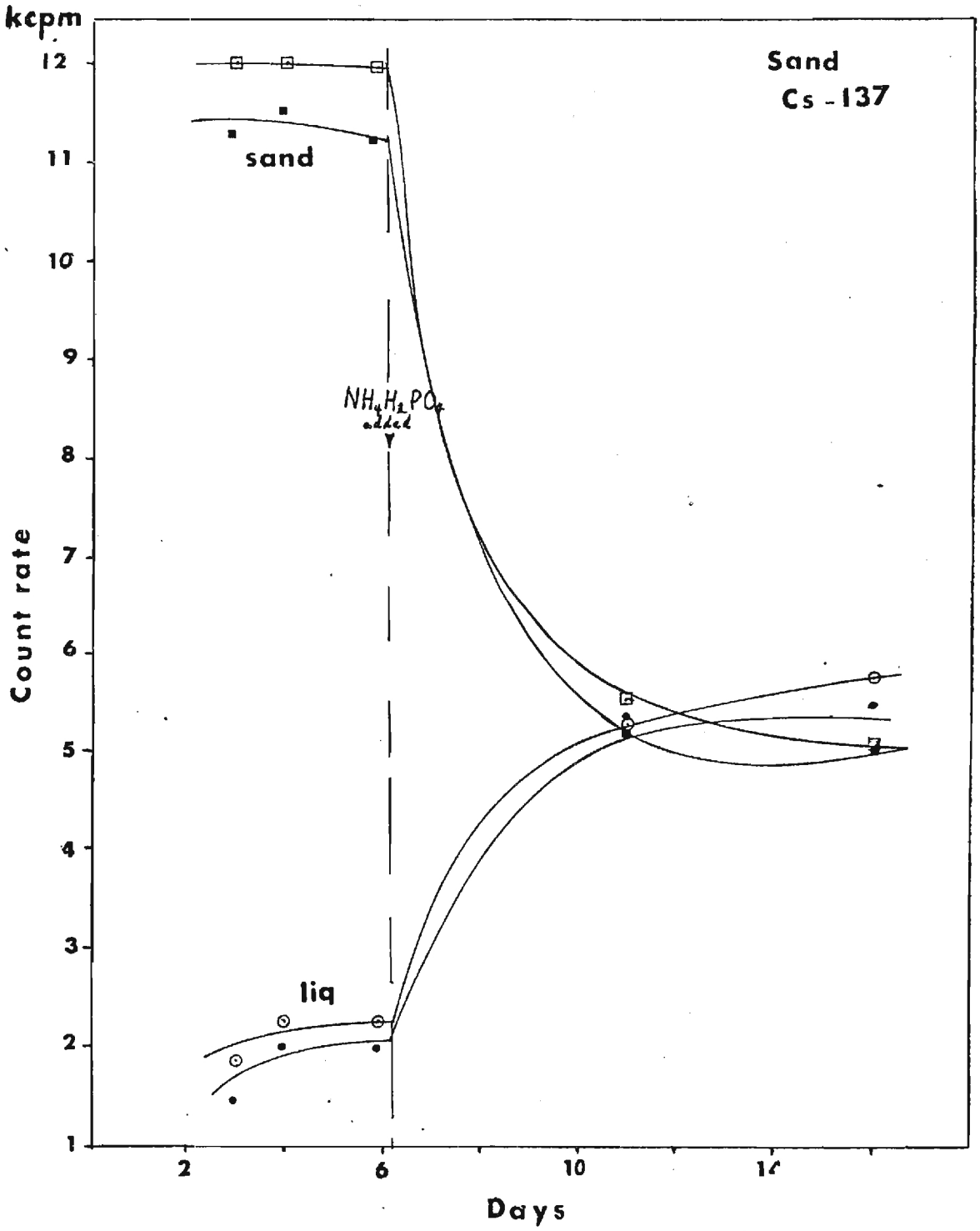


Figure 26. - Effect of Phosphate Addition on Cesium Adsorption on Sand

a. Adsorption of Tc-95m on Kaolin in the Presence of Sand from Equilibrated Water with Ammonium Phosphate Additions.

This test compared the K_d and K_a values obtained when varying amounts of phosphate were added to the solution either initially, before contacting the sand, or later, after sorption on the sand had occurred already. The results are tabulated in Table 17. Comparison with Table 16 shows some reduction in kaolin sorption, but little difference whether phosphate was added early or late, or how much.

b. Same Test, for Basalt and Kaolin.

This test is shown in Table 18; again little difference was observed for various amounts of phosphate. The amount of basalt was 0.5g in this test. The differences between the first and second set of results are ascribed to the continued change in pH which was observed for basalt and is shown in the following figures.

c. Adsorption of Cs-137 on Basalt and the Effect of Complexants.

A series of tests were run using Cs-137 as the tracer to observe the effect on adding sodium phosphate or EDTA to the solution. The results are shown in Figures 26 and 27. The steady change in K_a and pH in the water, which was not equilibrated initially, is dramatic in both cases. Adding either phosphate or EDTA changes both pH and Cs-137 sorption immediately; in fact, later tests showed that the change was almost instantaneous and not as gradual as these figures suggest.

Table 17. Effect of Phosphate Addition on Tc-95m Sorption on Sand and Kaolin from Equilibrated Water

$(NH_4)H_2PO_4$ Added (mg)	Time of Addition	K_d(sand) (ml/g)	K_a(sand) (ml/m^2)	K_d(kaolin) (ml/g)
10	init.	0.67	0.035	93
10	later	0.64	0.034	66
10	later	0.62	0.033	93
20	init.	0.58	0.031	70
20	init.	0.63	0.033	127
20	later	0.65	0.034	63
20	later	0.67	0.035	74
20	later	0.63	0.033	88
20	later	0.63	0.033	91
30	init.	0.65	0.034	96
30	later	0.60	0.032	76
30	later	0.67	0.035	69

Table 18. Effect of Phosphate Addition on Tc-95m Sorption on Basalt and Kaolin from Equilibrated Water

$(NH_4)H_2PO_4$ Added (mg)	Time of Addition	K_d(basalt) (mg/l)	K_a(basalt) (mg/m^2)	K_d(kaolin) (mg/l)
10	init.	0.98	0.052	76
10	init.	1.1	0.058	78
10	init.	1.06	0.057	70
10	init.	1.12	0.060	72
10	later	1.13	0.059	78
10	later	1.0	0.053	93
10	later (diff. pH)	3.5	0.18	89
10	later	2.0	0.11	76
20	later	1.3	0.068	71
20	later	2.0	0.10	77
30	later	1.7	0.09	105
50	later	1.43	0.075	82

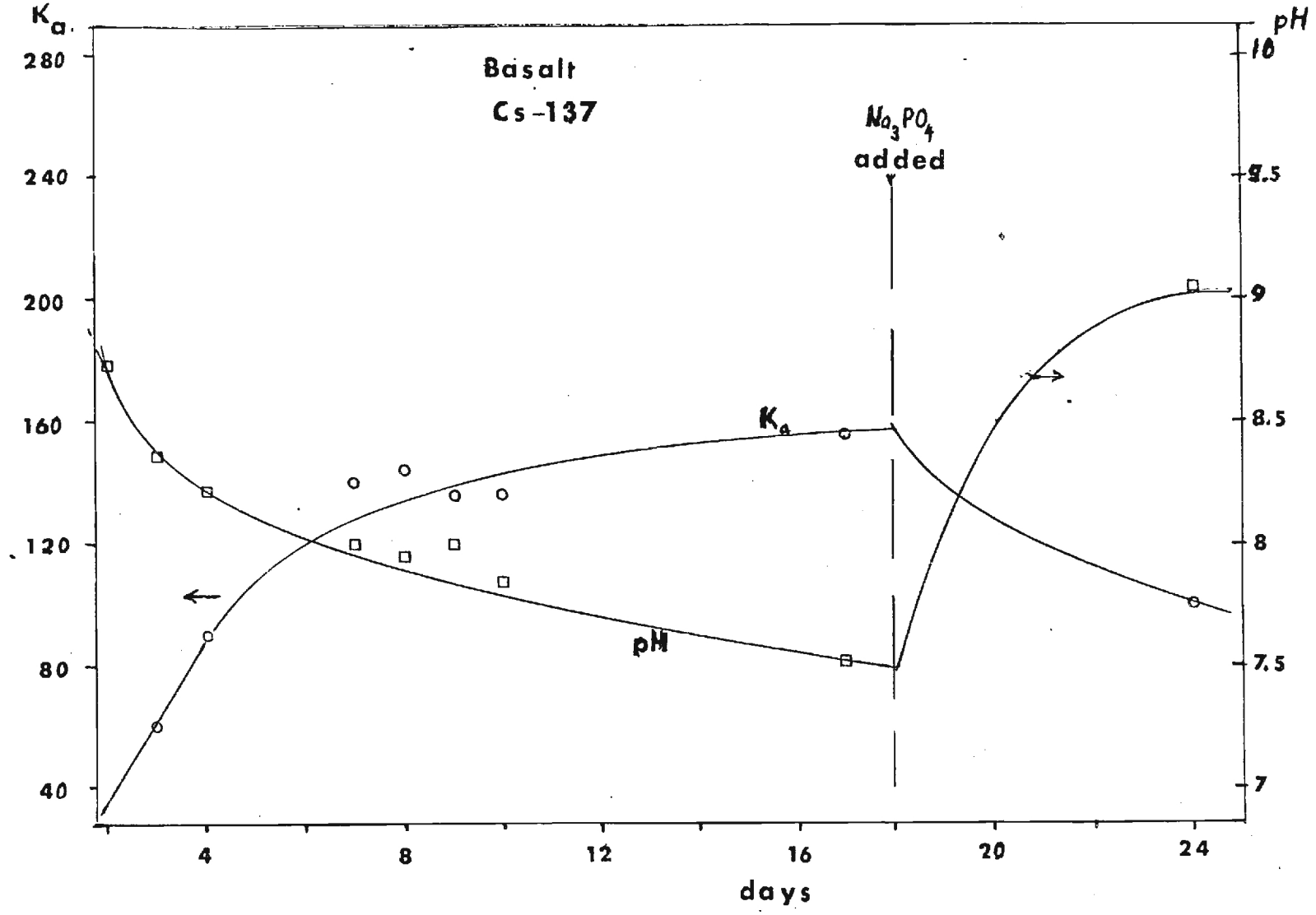


Figure 27. - Adsorption of Cs-137 on Basalt with Sodium Phosphate Added.

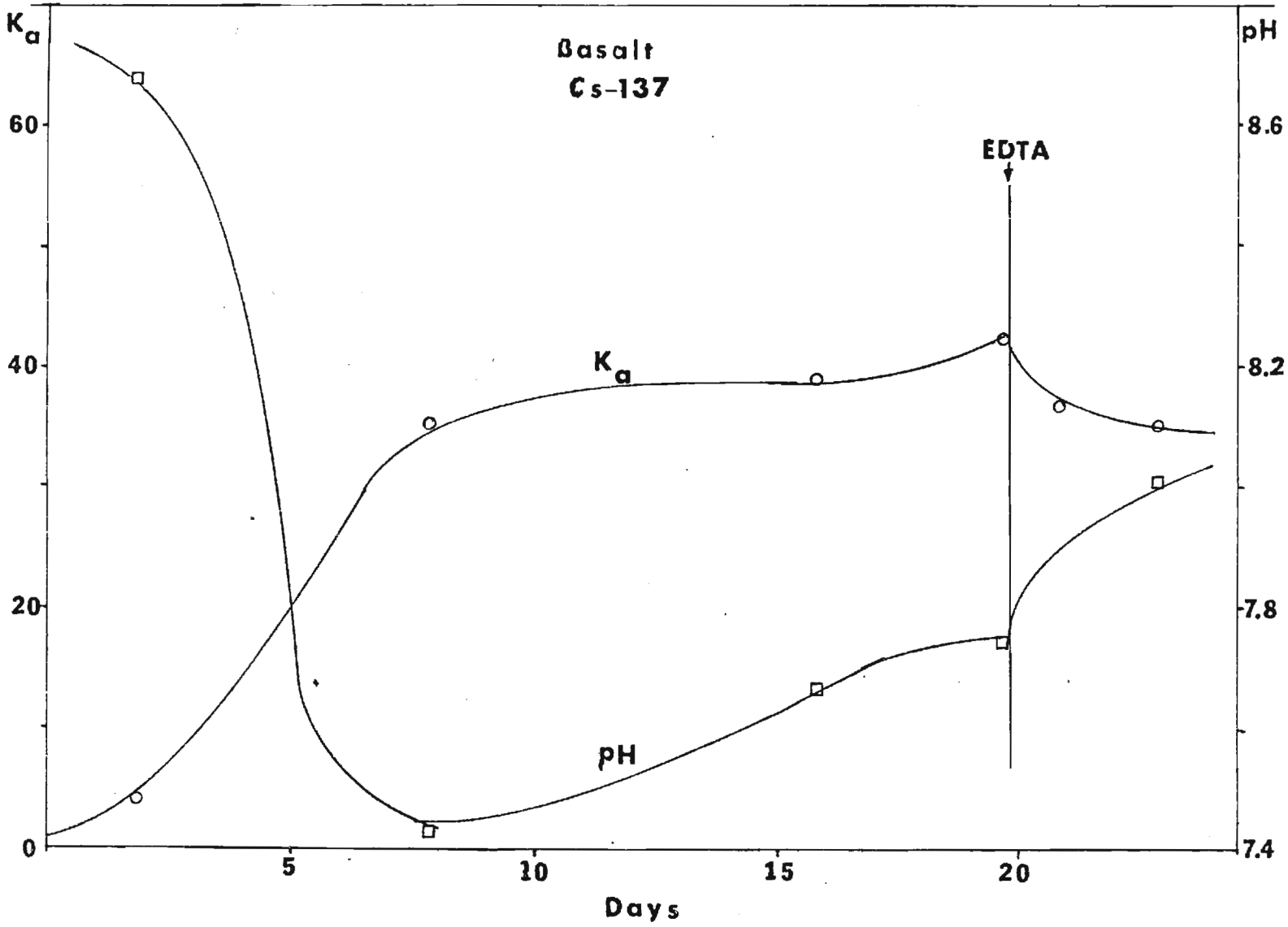


Figure 28. - Adsorption of Cs-137 on Basalt:EDTA Addition

d. Adsorption of Cs-137 on Limestone and Effect of Phosphate Addition.

Similar tests were conducted with 30-40 mesh limestone (marble). As Figure 29 shows, for duplicate runs equilibrium was attained more steadily, but again the addition of ammonium phosphate resulted in immediate desorption with a high proportion of the cesium staying in the solution.

To check the rate of change, four parallel tests were done adding ammonium phosphate to the Cs-137 - limestone solution after 18 days of equilibration. Figure 30A is representative of the results obtained. Samples were measured immediately before phosphate addition and 2 hours afterwards. The pH changed typically from 9.0 to 8.3.

e. Adsorption of Cs-137 on Sand and Effect of Phosphate Addition.

The same procedure was used with sand. Phosphate was added after 7 days contact when equilibrium had been reached and again a change in sorption on sand occurred immediately. Figure 30B is representative at this set of runs. pH changed from 8.97 to 8.30 typically, not enough by itself to account for the change in cesium uptake.

C. Studies on the Separate Effects of pH and Phosphate Additions on Cesium Sorption on Basalt.

Because in the previous experiments it was not immediately obvious whether the observed changes were the results of changing pH or the phosphate addition, a number of experiments were done to separate these effects.

All experiments had the following in common:

1. The mass of basalt was 0.500 gm in all cases.
2. The basalt was 30-40 mesh with sp. surface area $=8.99 \frac{m^2}{gm}$.

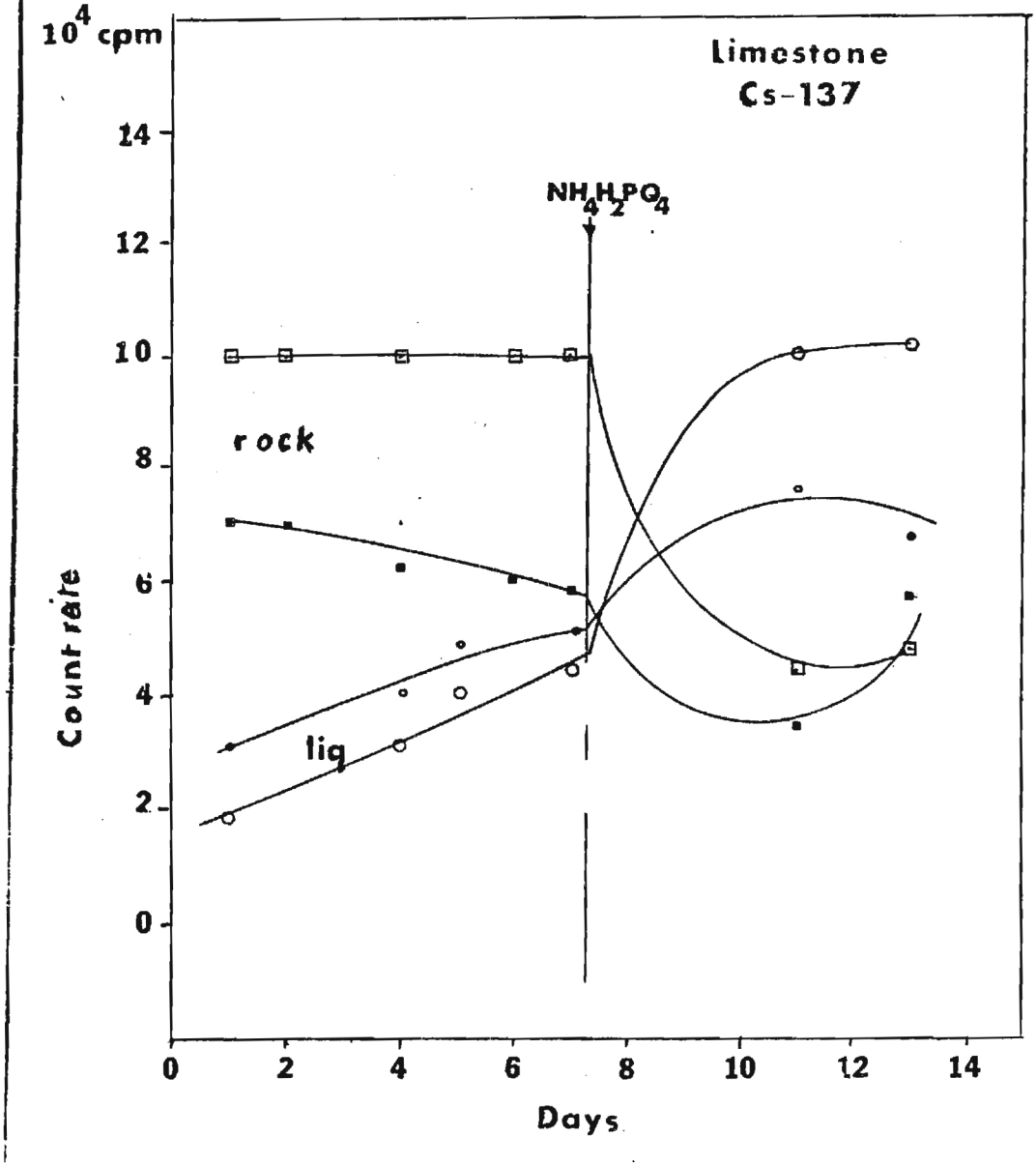


Figure 29. - Effect of Phosphate Addition on Cs Sorption on Limestone

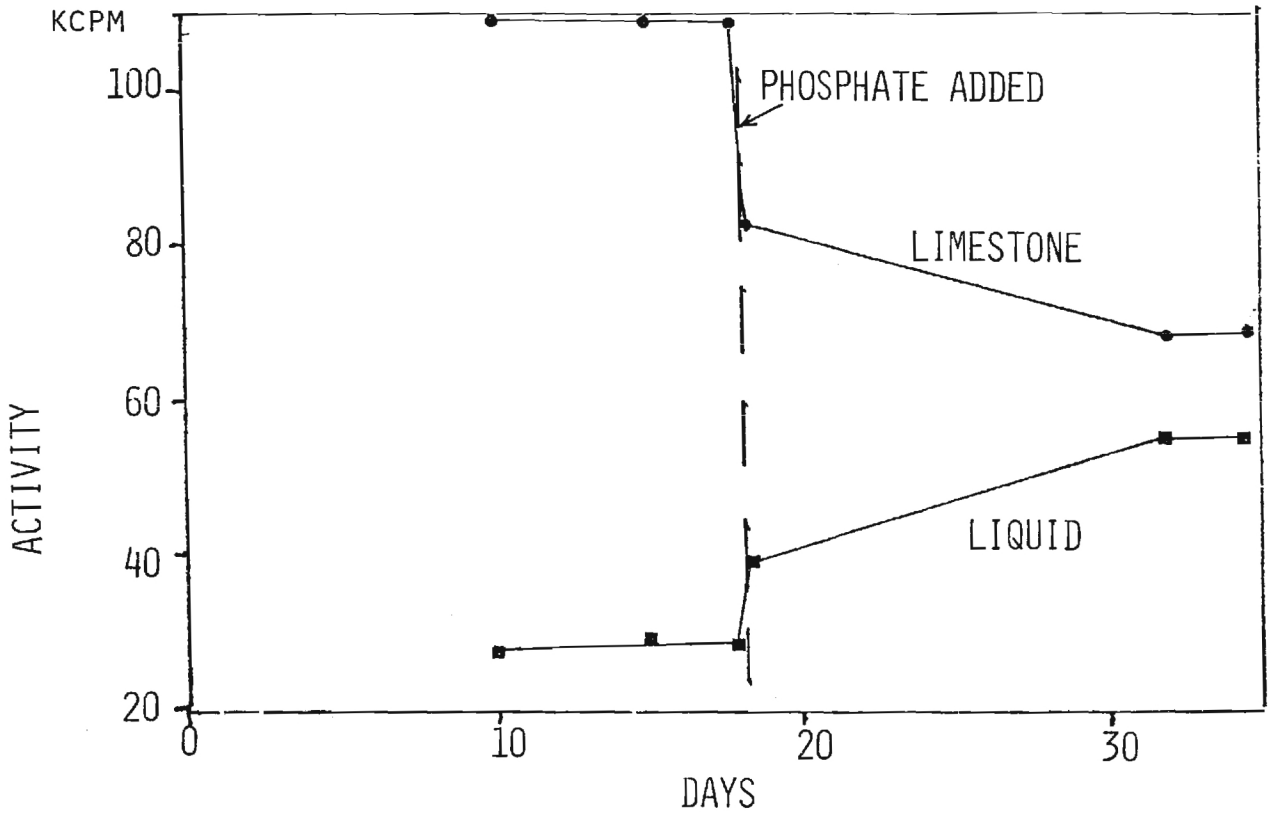


Figure 30A. - Cesium Adsorption on Limestone Before and After Phosphate Addition

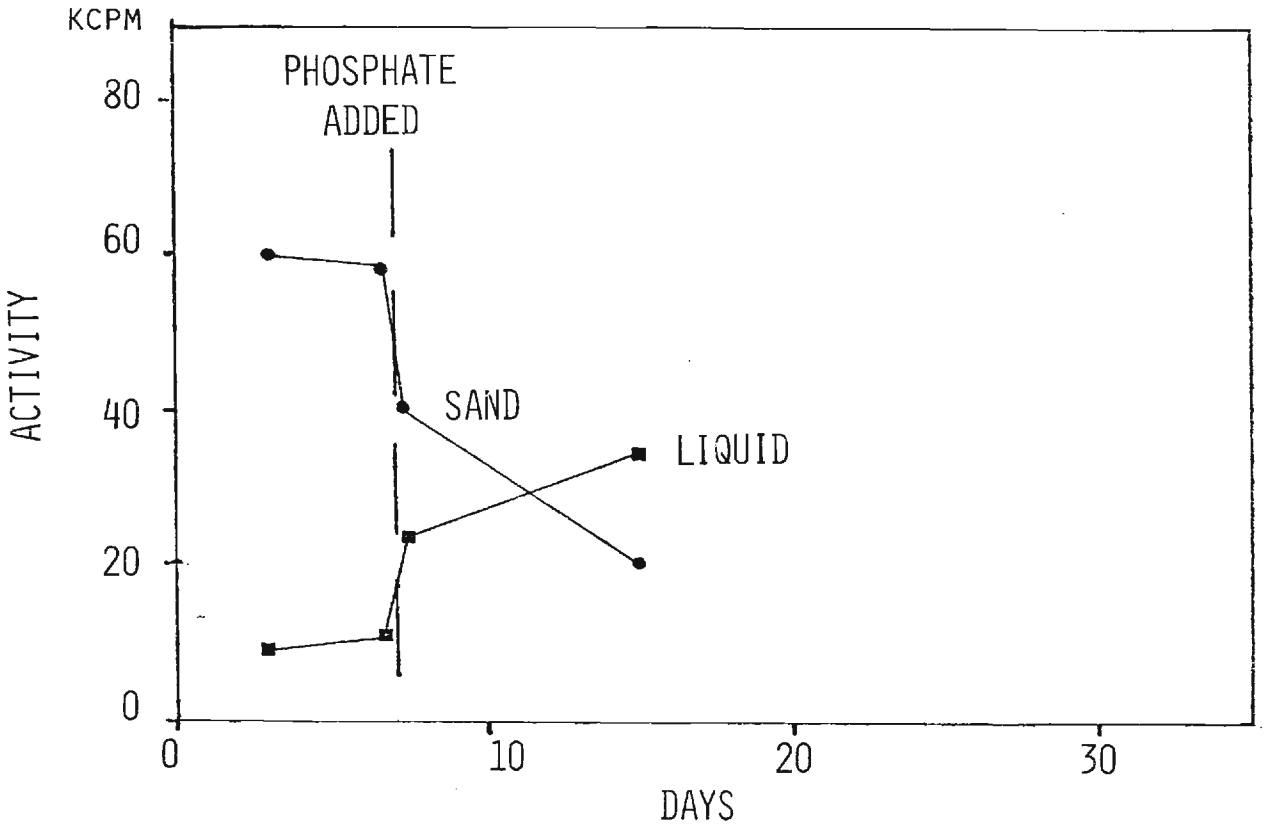


Figure 30B. - Cesium Adsorption on Sand Before and After Phosphate Addition

3. Total volume of liquid in each sample was 15 ml plus small variations for pH adjustment.

4. The water used was basalt equilibrated water in each experiment.

5. In each experiment the K_a value was determined by counting the solid basalt and a 5.0 ml aliquot of liquid at various time intervals. In each case the solid and liquid were temporarily separated for the counting.

Figure 31 illustrates two sets of experiments in which the pH was varied considerable, a long time was allowed to elapse for the basalt and water to equilibrate before phosphate was added on Day 40. The addition of phosphate made no apparent difference in tracer sorption. As it was thought that the decrease in K_a with time might be due to solubility of the basalt with time, the basalt was dried and weighed at the end of the experiment. No significant weight loss had occurred. At low pH the uptake of Cs on basalt was much lower and no intermediate peaking occurred, as for the high pH. The phosphate had the effect of raising the adsorption slightly, possibly due to an increase in pH.

In a different experiment, illustrated in Figure 32 1 mg of Na_3PO_4 was initially added to each sample. This apparently stabilized the basalt surface and prevented the erratic variations in K_a shown in the previous figure.

In two other experiments the cation in the phosphate and the concentration was varied. Figure 33 is representative of these tests. The value of K_a is seen to decrease with high phosphate concentrations. The K_a values with sodium phosphate are nearly twice as high as with comparable concentrations of ammonium phosphate. In the latter case samples reached

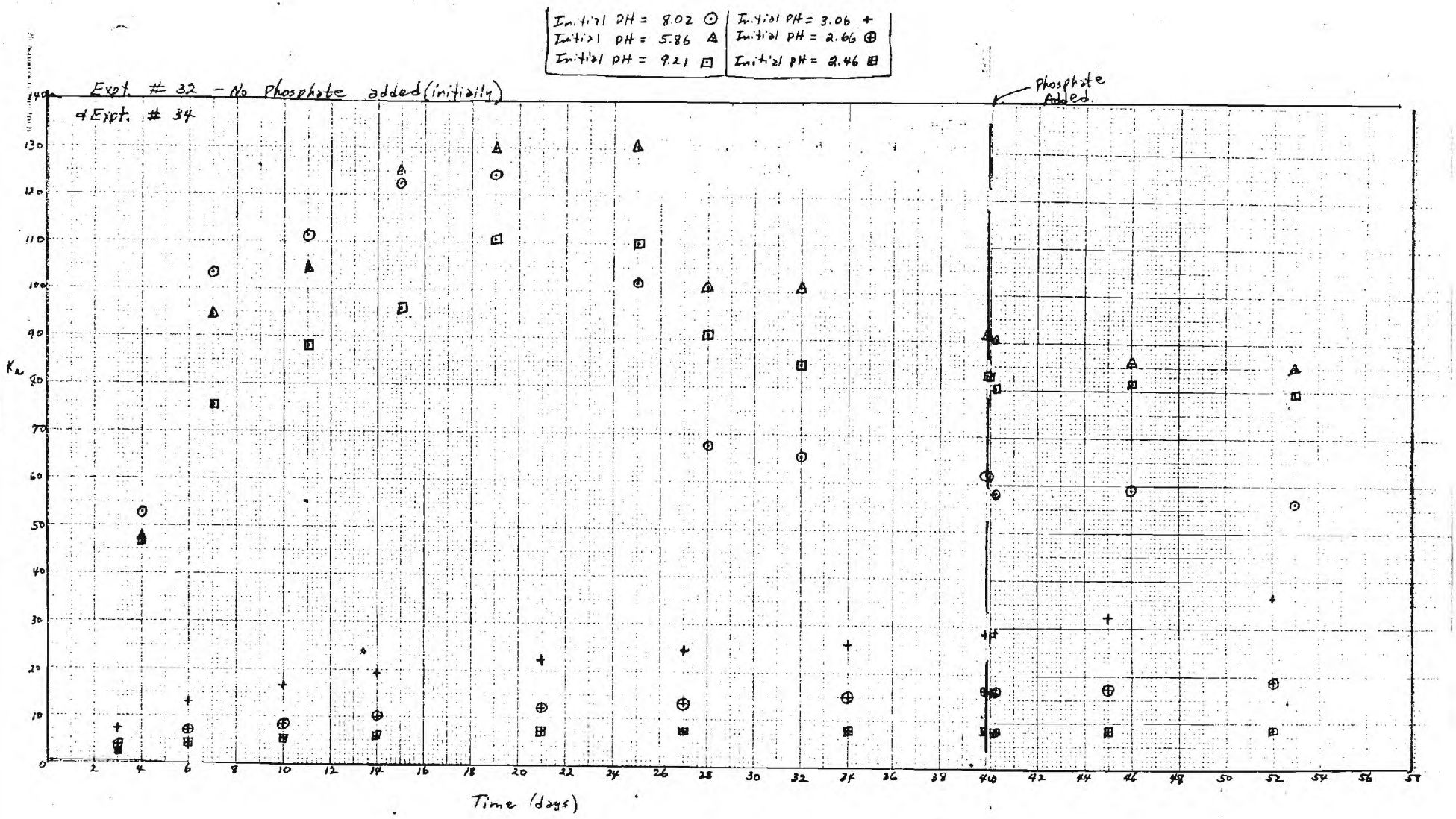


Figure 31. - Effect of pH on Cs-137 Sorption on Basalt and Phosphate Effectiveness

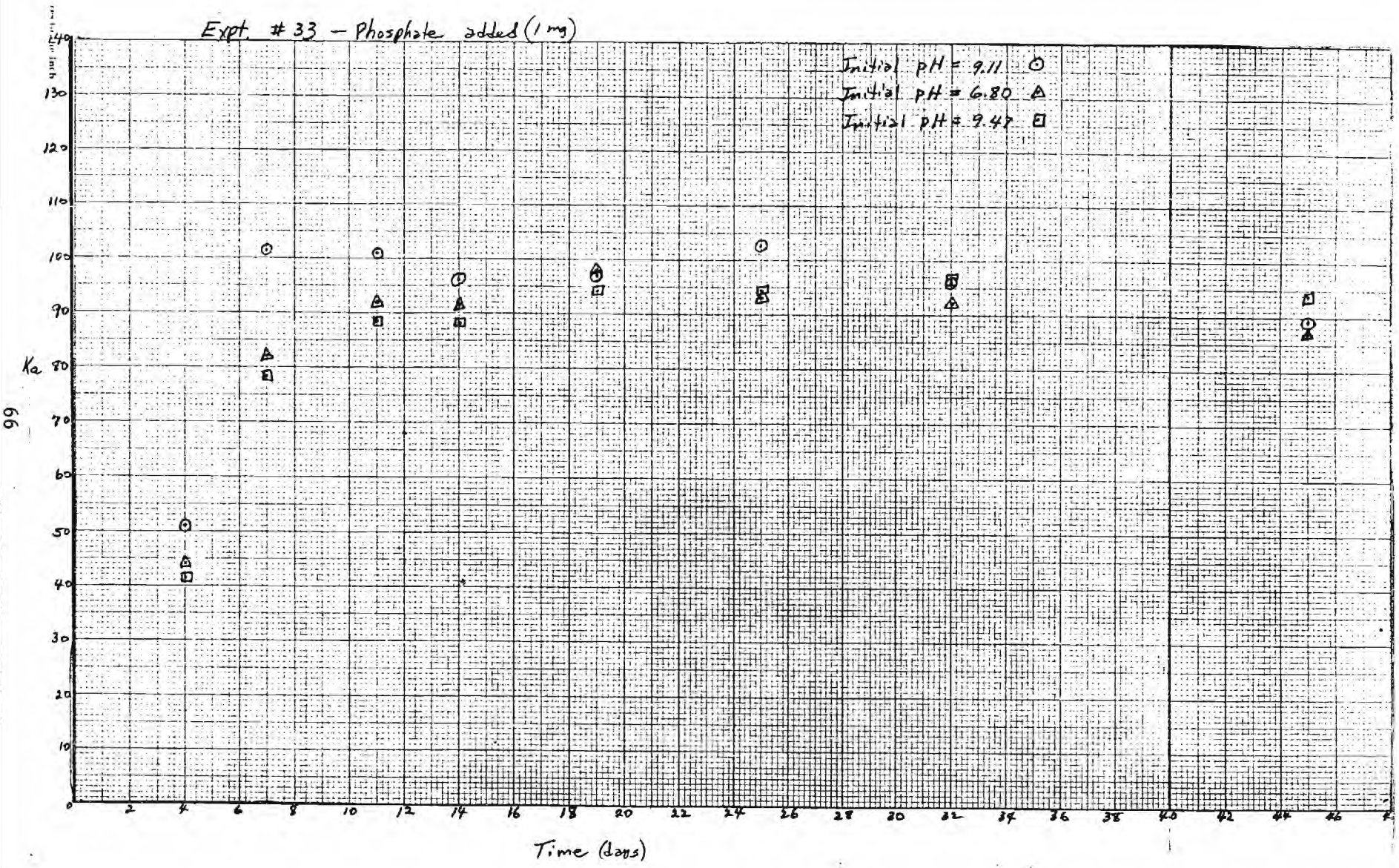


Figure 32. – Effect of Phosphate Pretreatment on Cs-137 Sorption on Basalt

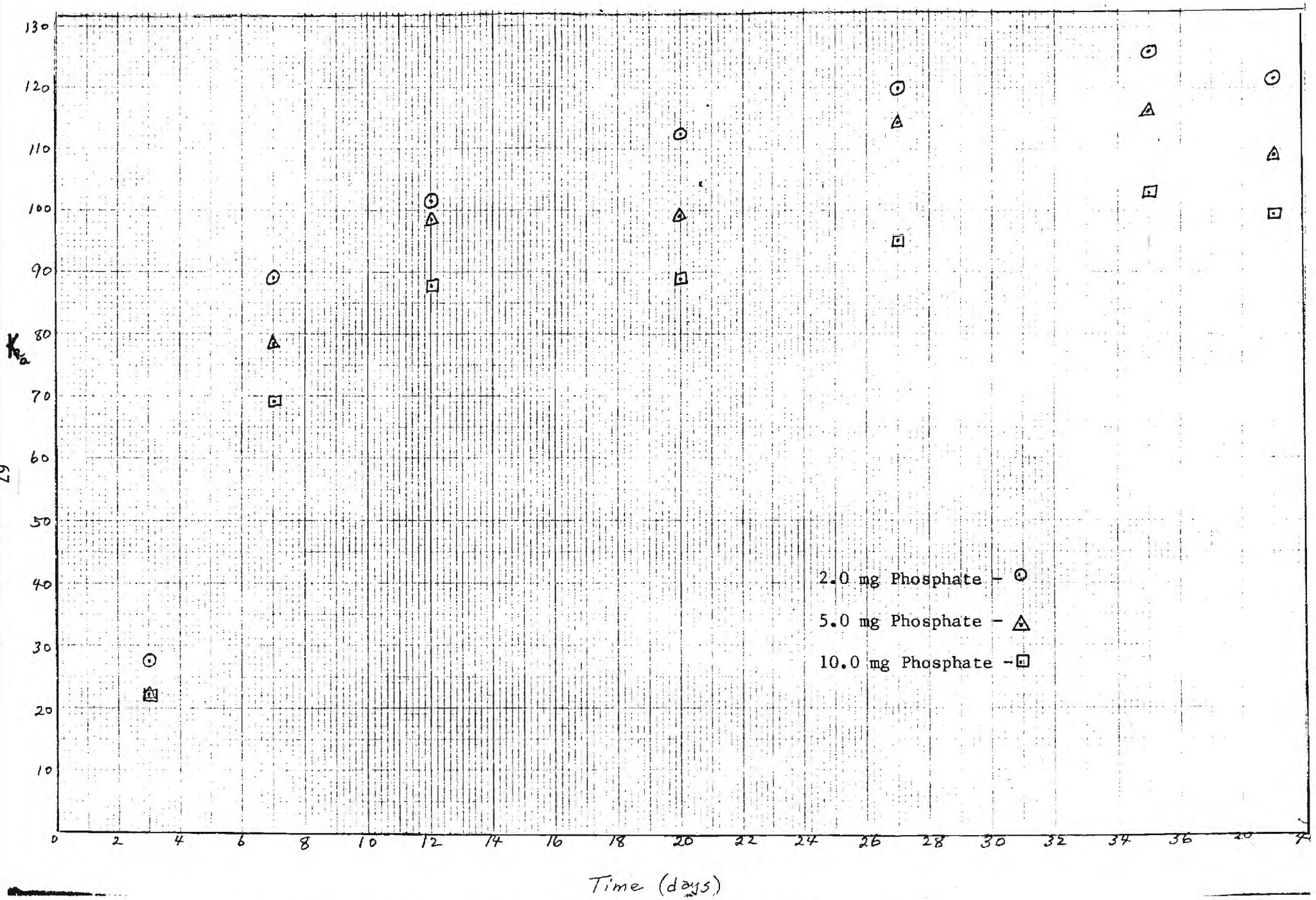


Figure 33. - Effect of Sodium Phosphate Addition on Cs Sorption on Basalt

a lower equilibrium K_a value sooner, perhaps due to the buffering effect of the NH_4^+ ions. The pH was adjusted the same, ~ 11.5, for all samples.

Finally, a series of six samples was checked over a 4-week period to see if the order in which reagents were added had any effect on the rate of adsorption of the Cs-137. The following were added in each case but in different order: Basalt (added first in each case) in all other expts., basalt was added last); 0.1 ml of Cs-137 Tracer; 0.1 ml of 0.1 m NaOH solu.; and 10 mg. of Na_3PO_4 contained in 0.1 ml of Soln. The order of addition to the basalt was:

Samples 1-2: Tracer, NaoH, Phosphate

Samples 3-4: NaoH, Phosphate, Tracer

Samples 5-6: Phosphate, NaoH, Tracer

Figure 34 shows the results. It appears that the tubes in which tracer was added first, adsorb somewhat more rapidly, but in time this is overcome and in the final reading the K_a for these samples was lower than the others. Other than that there are no spectacular results here. The order of addition does not appear to greatly affect the equilibrium.

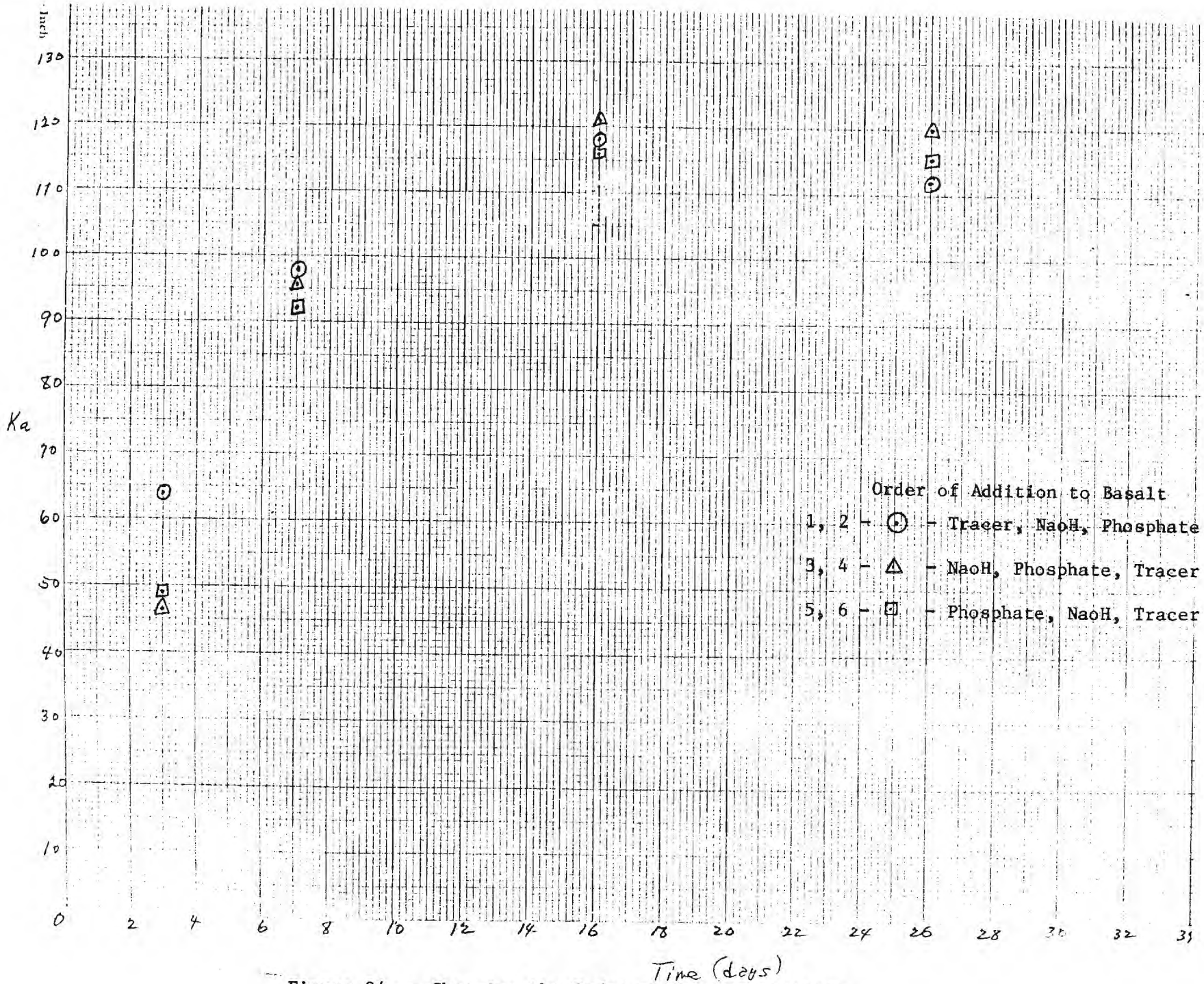


Figure 34. - Changing the Order of Reagent Addition

CONCLUSIONS

The work described here, though still somewhat preliminary in nature, has illustrated the importance of allowing for variable conditions of rainfall, drainage of repository trenches and the presence of complexing agents in assessing the impact of low-level waste disposal. Interesting results have been obtained on the migration of dissolved ions in soil under nonsaturated conditions and thus work should be extended to varying moisture profiles and site-specific conditions.

The work on fine particulate mobility has extended previous results and shown the existence of a chromatographic effect as well as an independent retardation process that depends on the rock material involved and any surface conditioning.

Work with phosphates and other complexing agents has indicated the significance of some of these materials in desorbing and remobilizing some adsorbed tracer materials, either through changes in pH or by complex formation or a synergistic effect. The tests showing slowly varying sorption conditions with time are not fully explained at this time; these effects seem particularly pronounced for basalt, which contains a variety of secondary minerals.

Overall, it is believed that the work described here has made a useful contribution to our understanding of waste ion migration in near-surface disposal sites, and it is hoped that this research can be carried forward to some more definitive conclusions. It is evident that particulates in groundwater may substantially modify waste migration conditions, as would the incursion of fertilizers, humic acids and other complexants. The important effects on nonsaturation conditions in the soil underlying the disposal trenches await additional studies before definitive conclusions can be drawn. All these aspects are expected to improve greatly our understanding of the processes that may lead to movement of both radioactive and nonradioactive wastes from burial sites.

REFERENCES

1. Public Law 96-573, "Low-Level Radioactive Waste Policy Act", 96th U.S. Congress, Washington D.C., 1980.
2. State Planning Council on Radioactive Waste Management, "Recommendations on National Radioactive Waste Management Policies", Washington D.C., 1981.
3. C.T. Duerksen, M. Mantell and G.P. Thompson (eds), "Toward a National Policy for Managing Low-Level Radioactive Waste", The Conservation Foundation, Washington D.C., 1981.
4. "Managing Low-Level Radioactive Wastes - A Technical Analysis", EG&G Idaho Inc., 1981.
5. J.A. Adam and V.L. Rogers, "A Classification System for Radioactive Waste Disposal - What Waste Goes Where?", Rept NUREG-0456, U.S. Nuclear Regulatory Commission, Washington D.C., 1978.
6. C.A. Little and L.E. Stratton (eds), "Modeling and Low-Level Waste Management: An Interagency Workshop", Rept. ORO-821, U.S. Dept. of Energy/NRC/EPA/USGS, 1980.
7. D.E. Large, R.S. Lowrie and L.E. Stratton (eds.), "Proceedings of the 2nd Annual Information Meeting: National Low-Level Waste Management Program", (unpublished), 1981.
8. M. Alexander, "Introduction to Soil Microbiology", Wiley, New York, 1977.
9. D. Hillel, "Soil and Water: Physical Principles and Processes", Academic Press, New York, 1971.
10. W.T. Lammers, "Biophysical Limnology: Separation of Suspended and Colloidal Particles from Natural Water", Enviromental Science & Technology, 1, 52-57, (1967).

11. P. Benes and V. Majer, "Trace Chemistry of Aqueous Solutions", Elsevier Scient. Publ. Co., Amsterdam, 1980.

12. G.G. Eichholz, T.F. Craft and A.N. Galli, "Trace Element Fractionation by Suspended Matter in Water", Geochim. Cosmochim. Acta, 31, 737-745 (1967).

13. G.G. Eichholz, G.F. Powell and T.F. Craft, "Waste Migration by Particulate Carriers", ANS Trans, 35, 66-68, (1980).

14. G.G. Eichholz (ed), "Mobility of Radioactive Waste Materials by Particulate Transport", Rept. NUREG/CR-2064, U.S. Nuclear Regulatory Commission, 1981.

15. G.G. Eichholz, H.E. Holloway and M.B. Downes "Effect of Complexing Ions on Remobilization of Radioactive Wastes", ANS Trans, 38, 158-159 (1981).

16. J. Bear, D. Zaslavsky and S. Irmay, "Physical Principles of Water Percolation and Seepage", UNESCO, Paris, 1968.

17. A. Hadas, D. Swartzendruber, P.E. Rijtema, M. Fuchs and B. Yaron, "Physical Aspects of Soil Water and Salts in Ecosystems", Springer-Verlag, New York, 1973.

18. "Permeability and Capillarity of Soils", ASTM Spec. Publ. STP No. 417, Am. Soc. for Testing and Materials, Philadelphia, 1967.

19. Letter from Dr. John E. Pinder, dated August 7, 1981.

20. M.D. Shaw and W.C. Arble, "Bibliography on Methods for Determining Soil Moisture", Engineering Research Bull. B-78, Pennsylvania State University, 1959.

21. H.F. Winterkorn (ed.) "Water and its Conduction in Soils", Highway Research Board Special Rept. 40, Nat Acad of Sciences - Nat. Research Council, Washington D.C., 1958.

22. B.G. Wahlig, "Transport of Suspended Matter Through Rock Formations", Ph.D. Thesis, Georgia Institute of Technology, Atlanta, 1980.

Appendix A

Source-Term Characterization for Buried Low-Level Nuclear Wastes

by

Homer E. Holloway

I. Introduction

The shallow land burial for low-level radioactive wastes (LLW) has been employed as a means of disposal since the days of the Manhattan Project. Before 1960 all low-level wastes were disposed of at AEC sites, regardless of where the wastes originated. By 1960 it became apparent that this was no longer feasible and commercial burial sites were put into the planning stages for future disposal of commercially generated wastes. These commercial sites were to be regional disposal sites on Federal - or state-owned land and were to be operated by private companies under AEC or Agreement State Licenses. The first of the commercial sites to be licensed was the one at Beatty, Nevada. Over the next 9 years, five additional sites were licensed at Maxey Flats, Kentucky (1963); West Valley, New York (1963); Richland, Washington (1965); Sheffield, Illinois (1967); and Barnwell, South Carolina (1971).

These facilities were located in remote areas and were believed to have good geologic conditions for burial of radioactive wastes. It was not anticipated that these wastes would migrate from the burial sites into the environment. The sites were licensed for the specific purpose of burial of low-level radioactive wastes and the conditions for license contained provisions for maintenance, inventory, health and safety and environmental monitoring. This also included perpetual care of the site as long as necessary after it closes operations.

The sites were not without problems. During the 1970's some of the sites were closed. The West Valley, New York site was the first to close in 1975 due to water management problems. The Maxey Flats, Kentucky site closed in 1977 after the Kentucky legislature imposed a 10 cents per pound

tax on burial and because of operational problems involving water management. The Sheffield, Illinois, site was exhausted in 1978 and was closed in 1979. The three commercial sites in Washington, Nevada and South Carolina are presently carrying the responsibility for all LLW generated in the U.S.

Some leaching problems have developed at some of the sites. At both West Valley and Maxey Flats water collected in the trenches and became contaminated due to poor trench design and site selection. In both cases only tritium has migrated off the site in surface and atmospheric waters. No contamination of off-site ground water has occurred at either site. The Sheffield site did not experience water management problems; however, recent geologic evidence indicates that there may be a problem in the future. Water management problems at both Maxey Flats and West Valley still persist after closure. Remedial programs are currently underway.

The whole idea of nuclear waste disposal has come under fire recently by the anti-nuclear forces. They tend to emphasize the risks, no matter how minute, and ignore the benefits of nuclear power. On the other hand, many of the pro-nuclear forces do just the opposite. There must be some reasonable intermediate ground.

The federal government has initiated a comprehensive program on radioactive waste management. One of the primary stated objectives of this program is to isolate existing and future radioactive wastes from the biosphere so that they will pose no significant threat to public health and safety. Obviously such a program must include looking at present methods of disposal and to consider what risks they present for future generations.

The object of this research is to attempt a characterization of the source-term for low-level radioactive wastes. This includes attempting to answer the following questions:

1. What are the sources and compositions of LLW?
2. How will the activities of these wastes vary with time?
3. What are the possible pathways for environmental contamination?
4. What are the barriers to prevent migration and how effective are they?
5. What are the estimated releases to the environment in 100 years, 500 years, 1000 years, etc.?

The problem is too complex to make accurate predictions; however, some realistic estimates can be made by making some believable assumptions.

II. Sources and Characteristics of Low-Level Radioactive Wastes

A. Producers of Wastes and Amounts Produced

The commercial LLW burial facilities were originally designed to receive radioactive wastes primarily from private industry, hospitals, and educational institutions that use radioisotopes. Over the years, after the opening of these sites, commercial nuclear power began a rapid growth rate and began sending increasing quantities of waste for burial. Of the total LLW shipped to commercial burial grounds, it is estimated that, by volume, the nuclear fuel-cycle wastes represent 60% and nonfuel-cycle wastes make up the remaining 40%. The total volume of fuel-cycle LLW is about 3.4×10^4 m^3. Some fuel-cycle LLW is generated at each step of the cycle: mining, milling, conversion of UO_2 to UF_6, enrichment, fuel fabrication, reactor operation, spent fuel storage (or reprocessing), facility decontamination, and decommissioning. At present the LWR power plants are the largest generators of LLW and fuel fabrication plants are second.

Most of the nonfuel-cycle LLW results from medical and academic applications. The remainder comes from industrial or other research applications. The medical type wastes comprise the major fraction of the institutional wastes with academic institutions contributing only about 1/8 of the total. Based on 1975 data, an estimated total annual volume of nonfuel-cycle commercial LLW is of the order of 2.2×10^4 m^3. Of this medical/biological type wastes make up 80% or 1.8×10^4 m^3. Other academic type wastes comprise 3-4% or 7.5×10^2 m^3, and industrial, research and other miscellaneous wastes make up the remainder (just under 15% or 3.2×10^3 m^3).

The amount of LLW produced annually is increasing rapidly, even though burial site capacity has decreased. A study[1] was made at the University of Maryland to estimate the rate at which the volume of waste is increasing. The estimated total waste volume shipped for burial by the study population in 1977 was 7771.1m^3. This was approximately 11% of the total LLW shipped during the year. Using additional data from previous surveys for 1972-79, it was possible to show that the waste volumes appear to be increasing linearly with time. The correlation coefficient for the least squares fitted line was 0.96 and the equation for the line is:

$$V = mx + b$$

where: V = Volume in m^3

$m = 639.74$

x = (year - 1900)

$b = 41621.63$

From this equation one should be able to make some predictions concerning the volume of waste in the future.

Other studies such as one by O'Connell and Holcomb[2] have made similar predictions. In this particular study, it was estimated that by the year 2000, the average annual volume of uncompacted LLW will be approximately 79×10^6 ft^3/year. One would not expect all the parameters used in such a projection to remain constant; however, it does point out the need for a large expansion in burial site capacity in the very near future.

B. Characteristics of Low-Level Radioactive Wastes

Low-level radioactive waste is usually described as having the following characteristics:

(1) Low enough beta-gamma activity levels so that no special provisions need to be made for heat removal.

(2) Penetrating radiation doses such that only minimal or no biological shielding or remote handling is necessary.

(3) Contain < 10n Ci/gm of transuranic α-emitters. This is a limit set by NRC and is presently under study for possible increase. An increase in this value would obviously increase the amount of LLW acceptable for burial.

Low-level wastes are categorized according to the isotopes they contain. Following the definitions in the Atomic Energy Act of 1954 the EPA office of Radiation Programs classifies the inventories from the burial sites as:

(1) Byproduct Material (reported in Curies) refers to any radioactive material (except special nuclear material and source material) obtained during the production or use of source or special nuclear material and includes fission products and other radioisotopes.

(2) Source Material (reported in lb or kg) refers to thorium, uranium, or any combination thereof, in any physical or chemical form. Source material does not include special nuclear material.

(3) Special Nuclear Material (reported in grams) refers to plutonium, Uranium-233, uranium containing more than the natural abundance of the 235 isotope or any material artificially enriched in any of these substances. Inventories[2] of these classifications of materials for the various burial sites are available.

Physical characteristics of LLW sent to burial grounds vary considerably. All generators of LLW have some dry wastes that are compactible or combustible. These include clothing, rags, paper, plastic, wood, etc. They also have a relatively small fraction that is not compactible or combustible, such as: contaminated equipment, tools, and glassware. In the fuel-cycle, dry LLW probably represents 30-40% of the total shipped to the burial site. Dry wastes are estimated to comprise 40-50% of the institutional LLW.

Prior to 1972, liquid wastes were shipped to burial sites to be stored until they were solidified. Since that time, these wastes are required to be solidified prior to shipment to the burial site. Most of the wet LLW wastes are generated by the cleanup of process streams in fuel-cycle operations. This process usually involves ion-exchange, filtration, and evaporation. The spent ion-exchange resins and filter sludges have for the most part been dewatered by decantation, filtration or centrifugation, placed in drums and sent to the

burial grounds. Sometimes absorbent materials such as vermiculite are added to take up any free liquid that might remain. With the more stringent requirements since 1972, the trend is toward immobilization of the resins and sludges by incorporating them in a solidification agent such as Portland cement or urea-formaldehyde polymer. In the future, other solid matrices, such as bitumen or unsaturated polyester resins may also be used. Solidification of the resins and sludges has the effect of increasing the LLS volume being shipped by a factor of 1.2 - 2, or greater, depending on the process used.

C. Radiological Characteristics of Low-Level Wastes

The radiological characteristics of LLW vary in accordance with their point of origin. The activity of defense and fuel fabrication LLW is mostly due to uranium and its daughters, although in some cases, mixed fission products may be present. For the most part, however, the distinguishing characteristic of these wastes is the dominance of the naturally-occurring long-lived alpha emitters.

The nuclear power plant wastes are characterized by their beta-gamma activity. Corrosion products circulating in the coolant are activated in the reactor core. The minute traces of uranium remaining on the fuel cladding after fabrication or failed fuel during reactor operation introduce mixed fission products into the coolant system. The activities of most concern in these wastes are those which have half-lives of several years, such as Co-60, Cs-137, and Sr-90. These are the activities that end up in filter sludges and ion-exchange resins during stream cleanup operations.

The radioactive species associated with medical/biological LLW usually have relatively short half-lives, generally being < 60 days,

if ^{3}H and ^{14}C are neglected. Other academic, industrial, research and other miscellaneous wastes contain a broad spectrum of radioactive species which are not easily classified.

A review of existing LLW waste facilities including their contents was carried out by Adam and Rogers[3]. These investigators found that, although the source of wastes may differ from site to site, the general characteristics and compositions of the actual wastes are generally similar. Therefore, it is reasonable to consider the wastes in a generalized Reference Containment Facility (RCF) to be approximately characteristic of all LLW burial sites. The characteristics of the RCF wastes are as follows. Since disposal facilities prohibit liquids, pyrophorics, explosives and hazardous biological or chemical forms of waste, we will consider only solid waste in the RCF. Table I lists the wastes and their initial inventories that have been determined by NRC to be representative of those expected to be disposed of in the future.

III. Disposal Methods

A. Solid Wastes

The burial procedures for LLW at all existing sites is similar. The solid wastes are placed in a container (usually a 55 gallon steel drum) and shipped to the burial site. Trenches are excavated at the site to depths of 8-10 meters. In humid climates the bottom of the trench may be filled with a porous drainage material, such as sand or gravel. The waste drums are placed in the trench to within 1 meter of the top. Once the filling of the trench is complete, the excavated soil is placed back on top, compacted, and mounded above the original surface to allow for future compaction and for proper drainage. Addi-

Table I

Representative Inventory for an RCF at Time of Closing

Nuclide	Average Inventory (Ci)	Average Concentration (Ci/m^3)
H-3	2.7×10^{6}	4.3
C-14	9.4×10^{4}	1.5×10^{-1}
Fe-55	1.6×10^{5}	2.6×10^{-1}
Co-60	4.8×10^{5}	7.7×10^{-1}
Sr-90	1.8×10^{3}	2.9×10^{-3}
Tc-99	1.2×10^{1}	1.9×10^{-1}
I-129	2.4	3.8×10^{-6}
Cs-135	1.2×10^{1}	1.9×10^{-5}
Cs-137	3.2×10^{5}	5.1×10^{-1}
U-235	2.0×10^{1}	3.2×10^{-5}
U-238	4.5×10^{2}	7.1×10^{-4}
Np-237	1.1×10^{-2}	1.8×10^{-8}
Pu-238	8.2×10^{1}	1.3×10^{-4}
Pu-239	1.1×10^{1}	1.7×10^{-5}
Pu-240	1.7×10^{1}	2.7×10^{-5}
Pu-241	4.2×10^{3}	6.7×10^{-3}
Pu-242	6.0×10^{-2}	9.5×10^{-8}
Am-241	8.2	1.3×10^{-5}
Am-243	5.2×10^{-1}	8.3×10^{-7}
Cm-243	1.6×10^{-1}	2.5×10^{-7}
Cm-244	4.8×10^{1}	7.6×10^{-5}

tional fill may be added later as further compaction occurs. Once the work at the site is completed it is revegetated to prevent erosion.

There are many treatment technologies available for volume reduction of LLW. Solid wastes can be subjected to compaction, combustion, meltdown casting, and dissolution and electroplating. Regulatory and economic factors may make volume reduction more attractive in the future. In general these treatments are well understood and are constantly being improved upon at DOE laboratories. They are available for commercial applications when needed.

B. Liquid Wastes

Since liquid wastes cannot be accepted for burial at commercial sites, they have to be solidified in some fashion.

Liquid scintillation counting is common in almost all institutions using radioactive materials for research, especially in the life sciences. Also common is the problem of disposal of the contaminated waste liquid scintillation fluid and vials. Various methods of disposing of these materials have been tried and it appears that some of the incineration methods are suitable. Typical liquid scintillation solutions consist of a solvent, such as toluene, xylene or dioxane plus a small amount of organic scintillator and up to 30% emulsifying agent and containing radioactive materials, such as H-3 and C-14. If the fluid is separated from the vials it can be burned as fuel in an incinerator or boiler after being mixed with fuel oil or it can be burned in an incinerator with other wastes. This produces some release of radioactive material to the atmosphere, but this is only a small fraction of the permissible levels according to 10CFR20.

The treatment of liquid solutions and wet solids produced from liquid radwaste treatment systems consists of three basic operations: (1) waste collection, (2) waste pretreatment, and (3) solidification. Here we will be concerned only with the solidification process.

During the solidification process, the wastes are incorporated with a solidifying agent to form a monolithic, free-standing solid. The basic solidifying agents used or proposed in the United States are (1) absorbents, (2) hydraulic cement, (3) urea-formaldehyde resin (UF), (4) other polymer systems, or (5) bitumen.

There are many factors that influence the integrity of the waste forms that are finally produced and shipped to the burial site. In the case of cement, for example, the correct amount of water must be included ($\sim$ 25%). Part of this water may already be present in the waste. Different formulations are used for different types of wastes[4]. The presence of borates or boric acid tends to prevent solidification. Certain additives, such as silicates can be added to improve setting properties[5]. Addition of clays can be used to decrease leachability[6]. Lime can be added to improve setting in boric acid wastes.

UF resin is an aqueous emulsion of urea and formaldehyde chemically combined to form linear polymeric chains. The resin consists of a viscous emulsion with water containing approximately 65% by weight of solids miscible with water but not with non-polar liquids. Aqueous liquid wastes may be mixed with UF emulsion at a waste-to-UF volume ratio of from 1:1 to 3:1, with 2:1 being typically recommended[7]. Optimum formulation depends on the waste properties.

Bitumen or asphalt is a mixture of high molecular weight hydrocarbons obtained as a residue from coal tar refining. Several types are available but the direct distillation product is the most widely suggested for radwaste solid[8]. Processes involving bitumen are not presently used in the U.S. but may be in the future.

Other polymer systems under study are water extensible polyester resins[9] such as one being marketed by the Dow Chemical Company[10].

IV. Pathways to the Environment

Burial sites for LLW are usually operated over a 10-20 year period. After this period of time, appropriate markers are installed, fences are maintained and environmental surveillance is continued, but perhaps with decreasing intensity. During the active operation time, funds are supposedly set aside from burial fees for "perpetual care" of the site after it is closed. Certainly this care will not continue forever and apparently nobody has defined just how long any care of the site will be expected to be maintained. Obviously the earthen barrier between the waste and the population will not remain intact forever.

There are several possible pathways by which the activity from the waste can end up in the biosphere. Its difficult to estimate probabilities for some of these because there just has not been enough accumulated experience.

A. Erosion.

It is estimated that erosion due to moving water will probably be less than 10 cm/1000 years[11]. Using this value for a site covered by 1.5-3 m of earth will produce a protection time to at least 15,000 -30,000 years. Using the isotopes proposed for the RCF and the appropriate half-lives we can determine the inventory of isotopes

remaining in that period of time. Table II shows the isotopes that would be present in appreciable quantities and their inventories after 15,000 years.

One can see that appreciable quantities of carbon-14 and rather less of several other isotopes would be present after erosion has completely removed the earthen cover from the burial site. If this is of real concern a thicker earth cover can be provided from the beginning.

B. Radionuclide Uptake by Roots

Over a period of 30 - 50 years after a site is closed, trees and shrubs will begin to grow over the area. These may put down roots deep enough to penetrate the waste. Water uptake by the roots will place activity in the tree. The activity spreads to the environment by falling leaves and other debris. This decays and is leached into the topsoil. In general the bulk of a plant's root system is contained in the upper 1 m of soil. It has been estimated[12,13] that only about 0.2% of the root biomass exist at depths greater than 1.5m.

A simulation technique[14] has been applied to Pu uptake in plants on a burial site. 2 Ci of Pu were assumed to be in the burial trench (0.8n Ci/g) with a cover of 1.5m and with no vegetation at t=0. It was assumed to be in an arid climate in which a forest growth matured in 150 - 200 years. At that time the Pu concentration at the surface was about 2×10^{-4} pCi/gm.

In a humid climate the concentration leveled out at about 3×10^{-4} pCi/gm. Natural fallout produces about $3\text{-}10 \times 10^{-3}$ pCi/gm for soils and plants. It is estimated that in 500 years uptake by plants will not give surface contamination distinguishable from surface contamination due to fallout.

TABLE II

Inventory of Waste Isotopes

Isotope	Inventory after 15,000 years (Ci)
C-14	1.5×10^{4}
Tc-99	1.1×10^{1}
I-129	2.0×10^{2}
U-235	2.0×10^{1}
U-238	4.5×10^{2}
Np-237	1.1×10^{-2}
Pu-239	7.2
Pu-240	3.5
Pu-242	5.8×10^{-2}
Am-243	1.3×10^{-1}

C. Burrowing Animals

Earth excavated by animals may be carried to the surface with contaminated waste. Some maximum typical depths for animal burrows[14] are given in Table III.

Almost no measures are taken against this kind of intrusion except the 1.0-1.5 m backfill. The container will help for a relatively short period. There is little or no information available concerning the probability of this event or its consequences, though presumably the main effects would be premature roof collapse or accelerated water seepage into the trench.

D. Leaching

Hydrologic studies must be performed, prior to establishing a burial site, to determine rates and directions of any migration that might occur from the buried waste. Environmental surveillance programs conducted during operations to gather additional data on site performance. If problems do develop during the operation of a site, hopefully, measures can be taken to correct the problem before decommissioning of the site.

Problems have developed at some sites. A number of studies at two commercial sites, Maxey Flats and West Valley, suggest that the following events have occurred: (1) wastes were buried and covered with earth; (2) precipitation infiltrated through the earthen cover, filled the trenches and soaked the wastes; (3) the water interacted with the wastes and formed a leachate, removing radioactive material from the waste; and (4) the leachate moved by one or more pathways to the uncontrolled environment.

Table III

Depths of Animal Burrows

Species	Maximum Depth
Prairie Dog	5m
Harvester Ant	3m
Pocket Mouse	2m
Pocket Gopher	0.6m
Mole	0.6m
Deer Mouse	0.3m

Dramatic changes could occur after decommissioning of a burial site that could significantly alter the rate of leaching. One such change could be a long-term increase in the rate of precipitation at the site. Methods are available for determining previous long-range climatic changes. An evaluation of climatic changes in the Western United States has been performed[15]. The most significant change that might occur is that a presently arid site might change to a humid site. If the burial site is properly designed with proper drainage of ground and surface water, there should be little concern for this kind of change over several hundreds or even thousands of years.

The problem of leaching seems to have been the most significant problem with burial sites up to the present time. For this reason, we will look further into this mechanism later on in this paper.

E. Excavation

One might assume that at some time in the future the contents of a burial site will be forgotten. The site might even be used as a development for building construction at some time. If this were to happen, the radionuclides could be excavated during site preparation. In this case we can only depend on the nuclides having decayed sufficiently to be of little hazard that time. The true nature of the hazard will depend on when the excavation occurs. Table II gives some indication of quantities of radionuclides that would remain after 15,000 years. The actual amount would probably be somewhat less than this due to leaching. However, a future excavator would have to be exceedingly unobservant to miss the character of the site he is digging up.

V. Calculations of Environmental Contamination from the Leaching Mode

In order to attempt to quantify the leaching rates of radionuclides from burial sites it was necessary to obtain some data on the nature of existing commercial and DOE burial sites. Table IV lists the various sites some corresponding meteorological data.

For purposes of calculation, it will be assumed that the burial sites at each of these locations is the standard site referred to previously as the RCF (Reference Containment Facility). This is basically a model shallow land burial facility whose characteristics were based on good engineering judgement. The RCF will contain the isotopes and quantities listed in Table I. These solid wastes are assumed to be contained in 55 gal. steel drums that are buried under a minimum of 1 m of compacted soil. It will be assumed that the soil over the top is sufficiently porous to allow percolation of rainwater into the trench and that the soil underneath is sufficiently impervious to allow for saturation of the trench during heavy rainfall with slow dewatering over a period of several days. These assumptions are not very realistic for some of the more arid sites.

Some important technical parameters of the RCF are as follows.

1. Site area - 2.0×10^6 m^2
2. Site capacity for waste - 6.3×10^5 m^3
3. Distance - pit to aquifer - 100 m
4. Fraction of pit volume occupied by waste - 0.5.

Obviously the first barrier to leaching is the 55 gal. drum used to contain the waste. The metal drum is usually given no credit for containment of activity in burial. The primary purpose of the steel drum is to provide ease of handling and for containment of activity before burial. However, the integrity of the container can be an important barrier to prevent migration of the activity for a short period of time.

Table IV

Existing Low-Level Waste Disposal Facilities

Location	Climate	Annual Rainfall (inches) (16)
*Hanford, Wa.	Semi-arid	7.4
Richland, Wa.	Semi-arid	7.4
Beatty, Nv.	Arid	4.7
*INEL, Id.	Semi-arid	9.1
Los Alamos, N.M.	Semi-arid	18.1
Sheffield, Ill.	Humid	33.5
Morehead, Ky.	Humid	37.4
*Oak Ridge, Tenn.	Humid	52.6
*Savannah River, S. C.	Humid	43.1
Barnwell, S. C.	Humid	43.1
West Valley, N. Y.	Humid	31.7

*DOE Sites.

An attempt was made to calculate this time in which the drum would prevent surface water from reaching the radioactive waste. In this calculation it was assumed that corrosion of the drum occurred from the outside only as a result of soil conditions.

Pitting is the type of corrosion of particular importance here. Soil as a corrosive environment is of greater complexity than any other. It is difficult to make accurate predictions because of the many variables. In a major investigation by NBS, corrosion of various metals in different soil conditions was studied over a 12 year period. It was concluded that soil conditions varied so greatly that an average rate for a given steel would have little value. Soil type was judged as a good criterion of corrosion rate. The most reliable parameter to estimate corrosivity of soils is the resistivity. The resistivity depends on temperature, moisture, dissolved salts, compactness of soil and the presence of inert materials, all the same elements that control the rate corrosion.

In the NBS study, an empirical equation was developed to relate the corrosion pit depth with time for various soil types.

$$P = K\left(\frac{T}{5.3}\right)^n$$

where:

P = pit depth in mils

K = Constant = mils on 0.4 ft.^{2} at 5.3 years.

T = Time in years

n = constant

The constants K and n were determined experimentally for a variety of soil types all over the United States.

In this present study an attempt was made to assign a soil type to each of the burial site locations based on similarities in geographical

location and rainfall. From this it was possible to assign values of K and n for each site and to calculate the expected time for site and to calculate the expected time for the pit depth to reach 50 mils, the thickness of a 55 gal. steel drum. Table V gives the results of these calculations.

Because of the rather arbitrary method of assigning soil types, these values should be considered very approximate. This does indicate that in most cases, one cannot expect the steel drum to contain the activity for more than a few years at the most.

Once the steel container is perforated, the solid waste inside is assumed to become saturated by rainwater percolating through the soil covering the waste. At this point leaching of the activity from the waste begins. In order to determine the rate at which leaching occurs, it is necessary to know the values for leaching constants (λ_L) for each of the radionuclides contained in the RCF. Very little information is available on leaching constants for many of the radionuclides. In the investigation by Adam et al.[3] it was necessary to evaluate soil samples taken below actual waste burial pits at Idaho National Engineering Laboratory (INEL) and to assume that nuclide contamination resulted from the migration of nuclides leaching according to the following expression:

$$L_r = \lambda_L I_m \exp(-\lambda_e t) \qquad (1)$$

where:

L_r = Leach rate in Ci/yr.

$\lambda_e = \lambda_L + \lambda_m$

λ_L = Radionuclide leach constant (yr^{-1}) for nuclide m.

λ_m = Radionuclide decay constant (yr^{-1}) for nuclide m.

I_m = Initial inventory of nuclide m.

Table V

Corrosion Rates of Steel Drums at Various Burial Sites

Location	NBS Soil Type No.	K	n	T (Yrs, for 50 mil pit)
Hanford, Wa.	13	63.7	0.18	1.4
Richland, Wa.	13	63.7	0.18	1.4
Beatty, Nv.	13	63.7	0.18	1.4
INEL, Id.	45	54.3	0.78	5.0
Los Alamos, N. M.	46	77.8	0.17	0.39
Sheffield, Ill.	30	32.1	0.53	12
Morehead, Ky.	7	31.1	0.46	15
Oak Ridge, Tenn.	22	57.7	0.21	2.7
Savannah River, S. C.	3	68.8	0.17	0.81
Barnwell, S. C.	3	68.8	0.17	0.81
West Valley, N. Y.	32	44.8	0.33	7.4

Thus, the values obtained for each nuclide in the RCF will apply to INEL only, because the annual rainfall at the various burial sites varies. If we make the assumption that the leach rate for each nuclide is proportional to the average annual rainfall as listed in Table IV, then the leach constants for each nuclide in the RCF at each site can be calculated. Table VI is a tabulation of the leach constants calculated in this manner.

On the basis of the calculated information in Table VI the least amount of leaching should occur at Beatty, NV and the most should occur at Oak Ridge, Tenn. Using the data in Table VI, the initial inventories in the RCF (Table I) and equation (1) the leach rates have been calculated for each radionuclide at various times in the future for the two extreme cases above. The results of these calculations are shown in Table VII. (Leach rates of $\sim 10^{-12}$ Ci/yr can be considered equal to zero).

If one now makes some further assumptions, it is possible to calculate the concentrations of each isotope in the leachate leaving the RCF. The total site area for the RCF was assumed to be 2×10^6 m^2. If we multiply this area by the average annual rainfall, converted to the proper metric units, this will give the total volume of water responsible for leaching. If we make the assumption that <u>all</u> of this water eventually ends up underground to leach and to dilute the leachate then we can calculate the maximum average concentration of the leachate.

$$C(\text{Ci/ml}) = \frac{L_r(\text{Ci/yr})}{V} \qquad (2)$$

C = Average concentration of leachate leaving RCF in some given year

L_r = Leach rate for the same year

V = Total volume of rainfall on the RCF during the year.

V = 2.4×10^{11} ml/year at Beatty, NV and 2.7×10^{12} ml/year at Oak Ridge, Tenn.

Table VI

Leach Constants (λ_L) for Isotopes in the RCF at Different Geographical Sites

Radionuclide	(λm)	Hanford & Richland, WA	Beatty, NV	INEL, ID	Los Alamos, N.M.	Sheffield, IL	Moreland, KY	Oak Ridge, Tenn.	Savannah River & Barnwell, S. C.	West Valley, N.Y.
H-3	5.62×10^{-2}	8×10^{-5}	5×10^{-5}	1×10^{-4}	2×10^{-4}	4×10^{-4}	4×10^{-4}	6×10^{-4}	5×10^{-4}	3×10^{-4}
C-14	1.21×10^{-4}	8×10^{-5}	5×10^{-5}	1×10^{-4}	2×10^{-4}	4×10^{-4}	4×10^{-4}	6×10^{-4}	5×10^{-4}	3×10^{-4}
Fe-55	2.57×10^{-1}	8×10^{-2}	5×10^{-2}	1×10^{-1}	2×10^{-1}	4×10^{-1}	4×10^{-1}	6×10^{-1}	5×10^{-1}	3×10^{-1}
Co-60	1.32×10^{-1}	8×10^{-2}	5×10^{-2}	1×10^{-1}	2×10^{-1}	4×10^{-1}	4×10^{-1}	6×10^{-1}	5×10^{-1}	3×10^{-1}
Sr-90	2.43×10^{-2}	8×10^{-3}	5×10^{-3}	1×10^{-2}	2×10^{-2}	4×10^{-2}	4×10^{-2}	6×10^{-2}	5×10^{-2}	3×10^{-2}
Tc-99	3.25×10^{-6}	8×10^{-5}	5×10^{-5}	1×10^{-4}	2×10^{-4}	4×10^{-4}	4×10^{-4}	6×10^{-4}	5×10^{-4}	3×10^{-4}
I-129	4.36×10^{-8}	8×10^{-2}	5×10^{-2}	1×10^{-1}	2×10^{-1}	4×10^{-1}	4×10^{-1}	6×10^{-1}	5×10^{-1}	3×10^{-1}
Cs-135	3.01×10^{-7}	8×10^{-4}	5×10^{-4}	1×10^{-3}	2×10^{-3}	4×10^{-3}	4×10^{-3}	6×10^{-3}	5×10^{-3}	3×10^{-3}
Cs-137	2.3×10^{-2}	8×10^{-4}	5×10^{-4}	1×10^{-3}	2×10^{-3}	4×10^{-3}	4×10^{-3}	6×10^{-3}	5×10^{-3}	3×10^{-3}
U-235	9.85×10^{-10}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
U-238	1.55×10^{-10}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Np-237	3.24×10^{-7}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Pu-238	7.89×10^{-3}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Pu-239	2.84×10^{-5}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Pu-240	1.06×10^{-4}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Pu-241	4.62×10^{-2}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Pu-242	1.79×10^{-6}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Am-241	1.60×10^{-3}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Am-243	9.40×10^{-5}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Cm-243	1.55	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}
Cm-244	3.87×10^{-2}	8×10^{-6}	5×10^{-6}	1×10^{-5}	2×10^{-5}	4×10^{-5}	4×10^{-5}	6×10^{-5}	5×10^{-5}	3×10^{-5}

Table VII

Leach Rates (Ci/yr) for Isotopes in the RCF at Different Times in the Future

Radionuclide	Beatty, NV				Oak Ridge, Tenn.		
	Im	100 yrs.	500 yrs.	1000 yrs.	100 yrs.	500 yrs.	1000 yrs.
H-3	2.7×10^{6}	4.8×10^{-1}	8.2×10^{-11}	5.0×10^{-23}	2.53	7.5×10^{-12}	3.5×10^{-22}
C-14	9.4×10^{4}	4.6	4.3	4.0	55	39	27
Fe-55	1.6×10^{5}	3.7×10^{-10}	1.7×10^{-63}	—	5.8×10^{-33}	—	—
Co-60	4.8×10^{5}	3.0×10^{-4}	7.2×10^{-36}	2.2×10^{-75}	4.7×10^{-27}	—	—
Sr-90	1.8×10^{3}	4.8×10^{-1}	3.9×10^{-6}	1.7×10^{-12}	2.3×10^{-2}	5.3×10^{-23}	2.6×10^{-35}
Tc-99	1.2×10^{1}	6.0×10^{-4}	5.8×10^{-4}	5.7×10^{-4}	6.8×10^{-3}	5.2×10^{-3}	3.9×10^{-3}
I-129	2.4	8.1×10^{-4}	1.7×10^{-12}	2.3×10^{-23}	1.3×10^{-26}	—	—
Cs-135	1.2×10^{1}	5.7×10^{-3}	4.7×10^{-3}	3.6×10^{-3}	3.9×10^{-2}	2.6×10^{-3}	1.8×10^{-4}
Cs-137	3.2×10^{5}	15	1.3×10^{-3}	1.0×10^{-8}	1.0×10^{2}	9.7×10^{-4}	4.9×10^{-10}
U-235	2.0×10^{1}	1.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}	1.2×10^{-3}	1.1×10^{-3}	1.1×10^{-3}
U-238	4.5×10^{2}	2.2×10^{-3}	2.2×10^{-3}	2.2×10^{-3}	2.7×10^{-2}	2.6×10^{-2}	2.5×10^{-2}
Np-237	1.1×10^{-2}	5.5×10^{-8}	5.5×10^{-8}	5.5×10^{-8}	6.6×10^{-7}	6.4×10^{-7}	6.2×10^{-7}
Pu-238	8.2×10^{1}	1.9×10^{-4}	7.9×10^{-6}	1.5×10^{-7}	2.2×10^{-3}	9.2×10^{-5}	1.7×10^{-6}
Pu-239	1.1×10^{1}	5.5×10^{-5}	5.4×10^{-5}	5.3×10^{-5}	6.5×10^{-4}	6.3×10^{-4}	6.0×10^{-4}
Pu-240	1.7×10^{1}	8.4×10^{-5}	8.0×10^{-5}	7.6×10^{-5}	1.0×10^{-3}	9.4×10^{-4}	8.6×10^{-4}
Pu-241	4.2×10^{3}	2.1×10^{-4}	1.9×10^{-12}	1.8×10^{-22}	2.5×10^{-3}	2.3×10^{-11}	2.0×10^{-21}
Pu-242	6.0×10^{-2}	3.0×10^{-7}	3.0×10^{-7}	3.0×10^{-7}	3.5×10^{-6}	3.5×10^{-6}	3.4×10^{-6}
Am-241	8.2	3.5×10^{-5}	1.8×10^{-5}	8.2×10^{-6}	4.2×10^{-4}	2.1×10^{-4}	9.3×10^{-5}
Am-243	5.2×10^{-1}	2.6×10^{-6}	2.5×10^{-6}	2.3×10^{-6}	3.1×10^{-5}	2.9×10^{-5}	2.7×10^{-5}
Cm-243	1.6×10^{-1}	3.9×10^{-74}			4.6×10^{-73}		
Cm-244	4.8×10^{-1}	5.0×10^{-8}	9.4×10^{-15}	3.7×10^{-23}	6.0×10^{-7}	1.1×10^{-13}	4.2×10^{-22}

Using this simple model, the concentrations of each of the isotopes in the leachate were calculated for both Beatty, NV and Oak Ridge, Tenn. the results of these calculations are shown in Table VIII.

Since much of wet low-level wastes is buried in the form of a solid matrix, it is of interest to determine how these solid waste forms will interact with leaching ground water in the future. Other forms of contamination such as animal burrows and tree roots will undoubtedly be of less concern with this type of waste. Information concerning leach rates from this type of waste form is only available on a limited number of isotopes at this time.

Leaching experiments[18] have been performed for simulated waste forms which employ waste/binder ratios typical of those employed for waste solidification. This data provides a direct intercomparison of the relative ability of various solidification agents to retain activity in leaching environments. Diffusion mass transport theory has been applied to the experimental leaching data considering the specimen as either a semi-infinite or finite medium.

The semi-infinite model implies that at least one portion of the specimen retains its initial composition throughout the test. This model reports the leach data as cumulative fraction release (x) times (V/S). where:

V = specimen volume

S = specimen external geometric surface area.

when the term (V/S) is used, leaching from a semi-infinite medium is independent of specimen size and geometry and the fraction released for different specimens can be compared readily. A 55 gal. drum used for waste disposal has a (V/S) ratio of about 10.8 cm.

Table VIII

Average Concentration (Ci/ml) of Leachate for Isotopes in the RCF

Radionuclide	Beatty, NV			Oak Ridge, Tenn.		
	100 yrs.	500 yrs.	1000 yrs.	100 yrs.	500 yrs.	1000 yrs.
H-3	2.0×10^{-12}	3.4×10^{-22}	2.1×10^{-34}	9.4×10^{-13}	2.8×10^{-24}	1.3×10^{-34}
C-14	1.9×10^{-11}	1.8×10^{-11}	1.7×10^{-11}	2.0×10^{-11}	1.4×10^{-11}	1.0×10^{-11}
Fe-55	1.5×10^{-21}	7.1×10^{-75}	—	2.1×10^{-45}	—	—
CO-60	1.2×10^{-15}	3.0×10^{-47}	9.2×10^{-87}	1.7×10^{-39}	—	—
Sr-90	2.0×10^{-12}	1.6×10^{-17}	7.1×10^{-24}	8.5×10^{-15}	2.0×10^{-35}	9.6×10^{-48}
Tc-99	2.5×10^{-15}	2.4×10^{-15}	2.4×10^{-15}	2.5×10^{-15}	1.9×10^{-15}	1.4×10^{-15}
I-129	3.4×10^{-15}	7.1×10^{-24}	9.7×10^{-35}	4.8×10^{-39}	—	—
Cs-135	2.4×10^{-14}	2.0×10^{-14}	1.5×10^{-14}	1.4×10^{-14}	9.6×10^{-16}	6.7×10^{-17}
Cs-137	6.25×10^{-11}	2.4×10^{-15}	4.2×10^{-20}	3.7×10^{-11}	3.6×10^{-16}	1.8×10^{-22}
U-235	4.2×10^{-16}	4.2×10^{-16}	4.2×10^{-16}	4.4×10^{-16}	4.1×10^{-16}	4.1×10^{-16}
U-238	9.2×10^{-15}	9.2×10^{-15}	9.2×10^{-15}	1.0×10^{-14}	9.6×10^{-15}	9.2×10^{-15}
Np-237	2.3×10^{-19}	2.3×10^{-19}	2.3×10^{-19}	2.4×10^{-19}	2.4×10^{-19}	2.3×10^{-19}
Pu-238	7.9×10^{-16}	3.3×10^{-17}	6.2×10^{-19}	8.1×10^{-16}	3.4×10^{-17}	6.3×10^{-19}
Pu-239	2.3×10^{-16}	2.2×10^{-16}	2.2×10^{-16}	2.4×10^{-16}	2.3×10^{-16}	2.2×10^{-16}
Pu-240	3.5×10^{-16}	3.3×10^{-16}	3.2×10^{-16}	3.7×10^{-16}	3.5×10^{-16}	3.2×10^{-16}
Pu-241	8.8×10^{-16}	7.9×10^{-24}	7.5×10^{-34}	9.2×10^{-16}	8.5×10^{-24}	7.4×10^{-34}
Pu-242	1.2×10^{-18}	1.2×10^{-18}	1.2×10^{-18}	1.3×10^{-18}	1.3×10^{-18}	1.2×10^{-18}
Am-241	1.5×10^{-16}	7.5×10^{-17}	3.4×10^{-17}	1.6×10^{-16}	7.8×10^{-17}	3.4×10^{-17}
Am-243	1.1×10^{-17}	1.0×10^{-17}	9.6×10^{-18}	1.1×10^{-17}	1.1×10^{-17}	1.0×10^{-17}
Cm-243	1.6×10^{-85}	—	—	1.7×10^{-85}	—	—
Cm-244	2.1×10^{-19}	3.9×10^{-26}	1.5×10^{-34}	2.2×10^{-19}	4.1×10^{-26}	1.5×10^{-34}

The semi-infinite solution for mass transport by diffusion from a homogeneous medium having a zero surface concentration for all $t > 0$ and neglecting nuclear decay is given by:

$$\frac{\Sigma A_n}{A_o}\left(\frac{V}{S}\right) = 2\left(\frac{D_e}{\pi}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \qquad (3)$$

where:

A_n = cumulative activity removed

A_o = initial activity

V = specimen volume

S = specimen geometric surface area

D_e = effective diffusivity

t = cumulative leach time.

When (cumulative fraction release) (V/S) is plotted versus $t^{\frac{1}{2}}$ this results in a straight line from which D_e can be determined. Actual graphs show an initial period in which the rate is higher due to surface effects. This effect may be modeled by determining the intercept of the curve. The corrected equation then becomes:

$$\frac{\Sigma a_n}{A_o}\ \frac{V}{S} = 2\left(\frac{D_e}{\pi}\right)^{\frac{1}{2}} t^{\frac{1}{2}} + B \qquad (4)$$

The term B can be thought of as an immediate release at $t = 0$. The following table (Table IX) presents data collected for three different radionuclides in various matrices and for different types of waste, the values for the slope $\left[2\left(\frac{D_e}{\pi}\right)^{\frac{1}{2}}\right]$, the intercept (B) and the predicted cumulative fractional release at 100 years. Nuclear decay is not considered in this data and all data points are plotted.

Table IX

Predicted Release Fractions for Cs and Sr from Solidified Wastes

Solidifying Agent	Waste Type	Waste/binder Wt. Ratio	Radionuclide	Slope ($cm/day^{1/2}$)	Intercept	Predicted Cumulative Fraction Release (100 yrs.)
Portland Cement (Type II)	3a	1.0	Cs	9.76×10^{-1}	3.75×10^{-1}	1.79×10^{-1}
			Sr	1.77×10^{-2}	1.68×10^{-1}	3.23×10^{-1}
			Co	1.84×10^{-4}	4.76×10^{-4}	3.34×10^{-3}
	2b	1.6	Cs	1.05×10^{-2}	1.19×10^{-1}	1.90×10^{-1}
			Sr	2.12×10^{-2}	1.17×10^{-1}	3.85×10^{-1}
Urea-Formaldehyde	3a	1.3	Cs	2.27×10^{-2}	3.49×10^{-1}	4.13×10^{-1}
			Sr	1.48×10^{-2}	2.36×10^{-1}	2.69×10^{-1}
	2b	2.0	Cs	1.50×10^{-3}	5.83×10^{-3}	2.73×10^{-2}
			Sr	1.26×10^{-2}	2.33×10^{-1}	2.30×10^{-1}
	1a	2.6	Cs	2.56×10^{-2}	3.06×10^{-1}	4.66×10^{-1}
			Sr	4.12×10^{-2}	-4.37×10^{-2}	7.48×10^{-1}
Vinyl-ester Styrene	3a	1.9	Cs	3.02×10^{-3}	7.78×10^{-3}	5.48×10^{-2}
			Sr	2.82×10^{-3}	1.75×10^{-2}	5.13×10^{-2}
			Co	8.54×10^{-3}	1.11×10^{-2}	1.55×10^{-1}

3a - BWR chemical regenerative waste (forced recirculation evaporation).

2b - Diatomaceous earth precoat filter cake.

1a - Bead resin waste (slurry).

In order to make the data in Table IX more relevant to what we are trying to accomplish in this paper, the following assumptions are being made:

(1) It is assumed that the average fraction leached per year (λ_L') under the experimental conditions is simply 10^{-2} (predicted accumulative fraction released in 100 years).

(2) The experimental procedure used to collect the leach data was apparently performed under continuously saturated conditions. In order to find approximate leach constants (λ_L) under conditions as they exist at actual burial sites, the following approximation is used. It is assumed that each one inch of annual rainfall will saturate the waste and that it remains saturated for a period of 6 days. This means that instead of the leach rate being continuously effective, it must be multiplied by the fraction $f = \frac{6(\text{average annual rainfall})}{365}$. Thus multiplying λ_L by f gives the effective leach constant characteristic of a given burial site.

Using these assumptions and corrections, the values of λ_L have been calculated for the cases illustrated in Table IX for Beatty, NV and for Oak Ridge, Tenn. In addition, average concentrations of leachate were calculated in the same manner as those listed in Table VIII. Initial inventories were assumed to be those in the RCF reduced by an appropriate fraction to account for the binder material that was included. The results of these calculations are given in Table X.

Table X

Leached Waste Concentrations from Periodically Flooded Wastes

Solidifying Agent	Waste Type	Waste/Binder Ratio	Radionuclide	Beatty, Nevada				Oak Ridge, Tennessee			
				λ_L	Concentrations (Ci/me) 100 yrs.	500 yrs.	1000 yrs.	λ_L	Concentrations (Ci/me) 100 yrs.	500 yrs.	1000 yrs.
Cement	3a	1.0	Cs-137	1.38×10^{-4}	9.05×10^{-12}	8.70×10^{-16}	8.20×10^{-21}	1.55×10^{-3}	7.89×10^{-12}	4.29×10^{-16}	2.00×10^{-21}
			Sr-90	2.49×10^{-4}	8.00×10^{-14}	4.36×10^{-18}	2.04×10^{-23}	2.79×10^{-3}	6.19×10^{-14}	1.22×10^{-18}	1.60×10^{-24}
			Co-60	2.58×10^{-6}	4.78×10^{-18}	5.60×10^{-41}	1.21×10^{-69}	2.89×10^{-5}	4.74×10^{-18}	5.50×10^{-41}	1.18×10^{-69}
	2b	1.6	Cs-137	1.46×10^{-4}	1.18×10^{-11}	1.12×10^{-15}	1.06×10^{-20}	1.64×10^{-3}	1.02×10^{-11}	5.33×10^{-16}	2.38×10^{-21}
			Sr-90	2.97×10^{-4}	1.17×10^{-13}	6.24×10^{-18}	2.85×10^{-23}	3.33×10^{-3}	8.61×10^{-14}	1.37×10^{-18}	1.37×10^{-24}
U - F	3a	1.3	Cs-137	3.19×10^{-4}	2.33×10^{-11}	2.08×10^{-15}	1.79×10^{-20}	3.57×10^{-3}	1.68×10^{-11}	4.06×10^{-16}	6.91×10^{-22}
			Sr-90	2.08×10^{-4}	7.60×10^{-14}	4.20×10^{-18}	2.00×10^{-23}	2.32×10^{-3}	6.10×10^{-14}	1.45×10^{-18}	2.40×10^{-24}
	2b	2.0	Cs-137	2.11×10^{-5}	1.87×10^{-12}	1.88×10^{-16}	1.88×10^{-21}	2.36×10^{-4}	1.82×10^{-12}	1.68×10^{-16}	1.51×10^{-21}
			Sr-90	1.78×10^{-4}	7.69×10^{-14}	4.30×10^{-18}	2.08×10^{-23}	1.99×10^{-3}	6.37×10^{14}	1.73×10^{-18}	3.38×10^{-24}
	1a	2.6	Cs-137	3.60×10^{-4}	3.35×10^{-11}	2.93×10^{-15}	2.48×10^{-20}	4.03×10^{-3}	2.31×10^{-11}	4.66×10^{-16}	6.29×10^{-22}
			Sr-90	5.78×10^{-4}	2.60×10^{-13}	1.24×10^{-17}	4.91×10^{-23}	6.47×10^{-3}	1.44×10^{-13}	6.48×10^{-19}	1.35×10^{-25}
V - ES	3a	1.9	Cs-137	4.23×10^{-5}	3.69×10^{-12}	3.66×10^{-16}	3.63×10^{-21}	4.74×10^{-4}	$3,52\times10^{-12}$	2.94×10^{-16}	2.35×10^{-21}
			Sr-90	3.96×10^{-5}	1.70×10^{-14}	1.01×10^{-18}	5.23×10^{-24}	4.43×10^{-4}	1.63×10^{-14}	8.20×10^{-19}	3.47×10^{-24}
			Co-60	1.20×10^{-4}	2.87×10^{-16}	3.21×10^{-39}	6.57×10^{-68}	1.34×10^{-3}	2.52×10^{-16}	1.73×10^{-39}	1.92×10^{-68}

XI. Conclusions and Sensitivity Calculations

An attempt has been made in this report to quantify the hazards due to buried low-level nuclear wastes. Two types of waste have been considered, solid waste buried in 55 gal. drums and wet wastes solidified in some type of matrix such as concrete or resin. Calculations were made on the basis of a Reference Containment Facility containing the types and quantities of wastes that are representative of those that will be buried in the future. Such wastes will undoubtedly contain many more short-lived isotopes; however, these have not been considered because they will have essentially decayed away before leach water can enter the waste container. Even though the container was not intended as a means of preventing loss of activity through leaching, calculations have shown that it is effective at least through several months. The time that the container actually contains the activity has not been included in any of the computations because it was short enough to be negligible compared with the shortest impact time interval considered (100 yrs).

Calculations of total activity released through the leaching process and the concentrations of leachate for the various isotopes have been attempted. These were carried out for time periods of 100 years, 500 years and 1000 years. Equations are included to permit calculations for other periods of time. Periods shorter than 100 years were not included because the burial sites will no doubt be under environmental surveillance for that period of time. During that time, problems can be corrected as they appear.

One important conclusion stands out in all the calculations. None of the calculated releases through the leaching process exceeds the standards set forth in 10CFR20 for concentrations in water. One would expect the

materials to be further diluted before entering surface streams, water supplies, etc.

There have been some important assumptions made and it is important to determine just how sensitive the calculated values are to these assumptions. Some of these assumptions are as follows:

(1) It was assumed that the leach constants (λ_L) were proportional to the average annual rainfall at each site. The calculated values were based on experimental values from INEL, Idaho. This seems like a reasonable assumption and can only be tested when experimental leach data is available from the other sites.

(2) For the purpose of calculating concentration, it was assumed that the released activity was diluted by the total rainfall on the area of the burial site. This is obviously not quite true. We do not know what fraction of the water runs off and what fraction percolates through the soil. Even so, this is probably not a bad assumption, because the total will eventually dilute the activity anyway by the time it reaches the surface or ground water.

If we consider that only a fraction of the water percolates through the soil, this should effectively reduce the leaching constant (λ_L) also. Let us consider a typical calculation to see what the effect would be. Assume an isotope with the following characteristics (Cs-137).

$\lambda_m = 2.3 \times 10^{-2}\ yr^{-1}$

$\lambda_L = 6 \times 10^{-3}\ yr^{-1}$

$I_m = 3.2 \times 10^{5}\ Ci$

$t = 100\ yr.$

Annual rainfall over site area = $2.7 \times 10^{12}\ cm^3$.

Using this data, we find the concentration of the leachate at 100 years to be 3.9×10^{-11} Ci/ml. If we now assume that only 10% of the water percolates through the soil, then $\lambda_L = 6 \times 10^{-4}$ yr^{-1} and volume of water $= 2.7 \times 10^{-11}$ cm^3. In this case we find the resulting concentration to be 6.7×10^{-11}, an increase by a factor of 1.7. Again this would be offset by a further dilution later on by the water that did not immediately enter the soil. One must also consider the very real possibility that water which drains away from one site may percolate through the soil at another nearby site. At any rate, this assumption does not appear to dramatically affect the results.

(3) Probably the most serious assumptions involve the leaching rate from wastes in a solidification matrix such as cement or polymeric resins. In order to obtain leach constants, it was assumed that each inch of rainfall on the burial site caused saturation of the waste and that this saturation remained for a period of 6 days. This obviously is only an educated guess; however, we can determine just how sensitive this guess is in the computations. Consider, for example, the case of Cs-137 in a solid concrete matrix with the following characteristics:

$\lambda_m = 2.3 \times 10^{-2}$

$I_m = 1.6 \times 10^{5}$ Ci.

$t = 100$ years

$\lambda_L' = 1.79 \times 10^{-3}$ yr^{-1} (measured under continuous saturation).

Annual rainfall = 52.6 inches.

Assuming the six-day saturation per inch of rainfall, we calculate λ_L by the following equation.

$$\lambda_L = \lambda_L' \left(\frac{6 \times 52.6}{365}\right) = 1.55 \times 10^{-3} \text{ yr.}^{-1}$$

This gives a leach concentration in 100 yr. of 7.9×10^{-12} Ci/ml. If we now change the number of days by a factor of 10 and assume that each inch of rainfall saturates for a period of 0.6 days, we find $\lambda_L = 1.55 \times 10^{-4}$ yr.$^{-1}$ and the concentration of leach at 100 years is 9.1×10^{-13} Ci/ml. Thus the concentration changes by a factor of 8.7. The true value probably lies somewhere in between the two values calculated. The method used should be considered as a first approximation used only because more information concerning the rate of percolation of water through the soil is unavailable. Obviously this will depend on soil conditions at each site and the methods used in preparation of the burial sites.

Even though these calculations indicate that the concentrations released after 100 years are within present standards, it cannot be concluded that there is no hazard due to leaching. If enough burial capacity is used there will eventually be a time when more and more radionuclides accumulate in the environment.

References

1. Beck, J. J., McCampbell, M. R. and Cooley, L. R., "A Profile of Institutional Radioactive Wastes Generated in 1977", in Proceedings of Health Physics Society Twelfth Midyear Symposium, Rept. EPA 520/3-79-002, 1979.

2. O'Connell, M. F., and Holcomb, W. F., 1974, "A Summary of Low-level Radioactive Wastes Buried at Commercial Sites Between 1962-1973, with Projections to the Year 2000", Radiation Data and Reports, 15, No. 12, 759, (1974).

3. Adam, J. A., and Rogers, V. L., "A Classification System for Radioactive Waste Disposal - What Waste Goes Where?", NRC Rept. NUREG-0456, FBDU-224-10, Utah, Ford, Bacon & Davis, 1978.

4. Tarnuzzer, E. C., 1976, "Nuclear Reactor Operations Wastes", Presented at the Annual Meeting of the American Nuclear Society, Toronto, Canada.

5. Heacock, H. W., and Riches, J. W., 1974, "Waste Solidification - Cement or Urea-Formaldehyde", 74-WA/NE-9, American Society of Mechanical Engineers, New York, NY.

6. Moore, J. G., Godbee, H. W., Kibbey, A. H., and Joy, D. S., 1975, Development of Cementitious Grouts for the Incorporation of Radioactive Wastes, Part I: Leach Studies, Report ORNL-4962, Oak Ridge National Laboratory, Oak Ridge, Tenn.

7. U. S. Energy Research and Development Administration, 1976, Alternatives for Managing Wastes from Reactors and Post-fission Operations in the LWR Fuel Cycle, Rept. ERDA-76-43.

8. Burns, R. K., 1971, "Solidification of Low- and Intermediate-level Wastes", Atomic Energy Rev., 9 (3), 547 (1971).

9. Subramanian, R. V. and Mahalingam, R., 1976, Immobilization of Hazardous Residuals by Encapsulation, Washington State University, Pullman, Wash.

10. Filter, H. E., 1976, The Dow System for Solidification of Low-level Radioactive Waste from Nuclear Power Plants, Dow Chemical Company, Midland, MI.

11. Fairbridge, R. W., 1968, Encyclopedia of Geomorphology, Reinhold Book Corp., New York, NY.

12. Wheeler, M. L., Smith, W. J., and Gallegos, A. F., 1977, "A Preliminary Evaluation of the Potential for Plutonium Release from Burial Grounds at Los Alamos Scientific Laboratory", LASL Report LA-6694-MS, Los Alamos, NM.

13. Romney, E. M., Mork, H. M., and Larson, K. H., 1970, "Persistence of Plutonium in Soils, Plants, and Small Mammals", Health Physics, 19, 487-491 (1970).

14. Carter, M. W., Moghissi, A. A., and Kahn, B. (ed.), 1979, Management of Low-level Radioactive Waste, Vol. 1, pp. 13-30, Pergamon Press.

15. Anteus, E., 1948, "The Great Basin with Emphasis on Glacial and Post-glacial Times", University of Utah Bulletin, 38, 168-191 (1948).

16. U. S. Weather Bureau, Climatic Summary of the United States - Supplement 1931-1952 - Climatology of the United States.

17. Romanoff, M., Underground Corrosion, NBS Circular 579, 1957.

18. Colombo, P. and Neilson, R. M., Brookhaven National Laboratory, Department of Nuclear Energy, Nuclear Waste Management Research Group; "Properties of Radioactive Wastes and Waste Containers", Progress Report # 10, NUREG/CR 0857, 1980.